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Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans in Houston Ship Channel Tissue and Sediment

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ABSTRACT

Concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) were measured in sediment, catfish, and crab tissue from 45 locations in the Houston Ship Channel in Texas in the Summer of 2002. Concentrations of individual 2378-substituted congeners ranged from 0.1 to 42,000 ng/kg dry wt, from 0.1 to 230 ng/kg wet wt, and from 0.1 to 260 ng/kg wet wt for sediment, catfish, and crab samples, respectively. OCDD concentrations in sediments were up to two orders of magnitude higher than those for the remaining congeners, but this signature was not observed in catfish and crab samples. Results from this study suggest that despite regulatory controls on discharges from pulp and paper mills, there has been little change over the last 10 years in dioxin concentrations in sediment and tissue from the Houston Ship Channel. Ongoing PCDD/PCDF inputs from urban and industrial areas along the channel as well as resuspension/desorption from contaminated sediments may provide a partial explanation for the lack of change. Simple correlation statistical and principal component analyses were undertaken.

Key words: dioxins; sediment; tissue; spatial trends; fingerprint analysis

INTRODUCTION

POLYCHLORINATED DIBENZO-*P*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), hereafter referred to as "dioxins," are two of the most common of the highly toxic groups of polychlorinated-dibenzene compounds. These toxins are tricyclic, planar, chlorinated compounds that have similar chemical properties. Dioxins are nonpolar, poorly water-soluble, lipophilic, stable chemicals (Alcock and Jones 1996; Rappe, 1996) that are extremely persistent in the environment and can affect human health at low concentrations. Chemicals within this group have been identified as potential carcinogens and endocrine disruptors (Aylward *et al.*, 1996; Neuberger *et al.*, 1999).

Dioxins are not specifically manufactured products; rather, they occur as a byproduct from activities such as incineration (of products containing chlorine), chemical

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processing, and bleaching of paper pulp. The environmental deposition of dioxins and furans is thought to have been quite low before 1930. Sediment core studies showed that dioxin levels began to increase in the 1930s and peaked around the 1970s, but have since steadily declined (U.S. Environmental Protection Agency, 2000). Dioxins, emitted into the air or discharged through wastewater effluent, eventually reach receiving water bodies either through point source discharges or through diffuse nonpoint sources such as runoff and dry and wet deposition of atmospheric emissions.

A number of studies in the general literature have documented the widespread presence of these compounds in sediment and fish and crab tissue from receiving water bodies (Czuczwa and Hites, 1984; Oehme *et al.*, 1990; Bopp *et al.,* 1991). Of particular interest are studies of dioxin in sediment and tissue from industrial areas, since the Houston Ship Channel (HSC), the subject of this paper, is home to one of the largest industrial complexes in the United States. Table 1 summarizes the levels of dioxins in sediment and tissue observed in other industrialized areas around the world. As can be seen in Table 1, reported levels in sediment have ranged from 0.3 to 1980 ng total equivalent concentration (TEQ)/kg-dry wt, and tissue from 0.4 to 2,783.8 worldwide. A brief summary of the key findings from these studies follows.

Bopp *et al.* (1991) found that levels of OCDD from sediment samples from locations adjacent to an industrial site in Newark, NJ, where chlorinated phenols had been produced were many times higher than those of 2378-TCDD. Evers *et al.* (1993) analyzed for dioxins in sediments from two depositional zones of the North Sea for dioxins and concluded that these compounds originated mainly from industrial operation discharges related to the production of chloroaliphatic compounds and a chloralkali plant in the area (OCDF dominated profile), and that atmospheric deposition was significant only for remote marine environments. Sakurai (2003) identified combustion processes, impurities in PCP (pentachlorophenol), and impurities in the herbicide CNP (chlornitrofen) as the major sources to the Kanto Region in Japan.

Bonn (1998) found significantly higher concentrations of dioxins in urban/industrial areas than those from reference, agricultural, and mixed-use areas and reported and increasing dominance of highly chlorinated compounds where human and industrial activity increased. Foster *et al.* (1999) measured higher dioxin concentrations in fish collected near a bleached kraft pulp mill than those near a wood treating facility but found the opposite in sediment. Sakurai *et al.* (1996) found that 1368- and 1379-TCDDs accounted for more than 95% of the TCDDs and that 2468-TCDF was the predominant TCDF isomer in sediment and tissue samples from a Japanese lake. These observations correspond to the main components of the PCDD/F impurities of the herbicide CNP leading Sakurai *et al.* (1996) to conclude that CNP was one of major sources of the PCDD/Fs in the study area. Jimenez *et al.* (1998) analyzed dioxins in crabs and sediments from the Venice and Ortebello Lagoons in Italy. They found the highest dioxin concentrations in an area characterized by high industrial impact. In addition to increased levels of dioxins, the above-referenced studies showed different PCDD/PCDF homolog profiles for sediment and tissue collected from the same locations possibly due to selective uptake or metabolism of PCDD/Fs, or variable sediment contamination leading to variability in tissue accumulation.

While the above referenced studies have documented the increased levels of dioxins in sediment and tissue in

Table 1. Dioxin concentrations in sediment and tissue from other studies.

Location	*Sediment*	*Crab*	*Fish*	*Reference*
North Sea	5–32[a]			Evers *et al.*, 1993
Catalonia, Spain	0.4–39.2[a]			Eljarrat *et al.*, 2001
Willamette Basin, Oregon	80–7000[c]		10–140[d]	Bonn, 1998
Venice and Ortebello Lagoons, Italy	0.4–35.1[a]	1.5–5.7[b]		Jimenez *et al.*, 1998
Facility and in the vicinity of a pulp mill	0.3, 144.5[a]		3.4, 7.9[b]	Foster *et al.*, 1999
Vicinity of magnesium plant in Norway		26.2–2783.8[b]		Oehme *et al.*, 1990
Tittabawassee River	1.7–1980[a]			Hilscherova *et al.*, 2003
Japanese Lake	0.8–28.9[a]		0.5–3.4[d]	Sakurai *et al.*, 1996
British Columbia Coast	43–59,000[c]		19–33,000[d]	Yunker *et al.*, 2002
Houston Ship Channel	0.1–443.8[a] 93.2–49,833[c]	0.4–16[b] 6.2–308.3[d]	0.42–41.1[b] 0.36–309.9[d]	This study

TEQ calculated using the World Health Organization scheme for normalizing dioxin concentrations based on risk (Van den Berg *et al.*, 1998); [a]TEQ concentrations in ng/kg-dry wt; [b]TEQ concentrations in ng/kg-wet wt; [c]Total PCDD/F concentrations in ng/kg-dry wt; [d]Total PCDD/F concentrations in ng/kg-wet wt; The Newark Bay data were not included because Bopp *et al.* (1991) did not report results for all 17 2,378-substituted congeners.

industrial areas, very few investigated the temporal variations of these levels, probably due to the time and expense involved in sampling for dioxin. There is, however, an increasing interest in understanding dioxin concentration changes over time especially in areas where source controls have been enacted (e.g., pulp and paper mills) and in areas where fish consumption advisories exist due to dioxin contamination. Yunker *et al.* (2002), for example, analyzed dioxin concentrations in sediment and crab tissue from sites along the British Columbia (BC) coast to evaluate changes due to source controls at pulp and paper mills. They compared their measured dioxin concentrations to available PCDD/PCDF data for coastal BC from 1987 to 1995 and found that total PCDD/PCDF concentrations for Dungeness crab hepatopancreas had declined, whereas total PCDD/PCDF concentrations in sediment showed less change over time. Their fingerprint analyses also showed more changes over time for crabs than for sediment samples. Yunker *et al.* (2002) attributed the lack of change in sediment dioxin levels partially to the presence of active PCDD/PCDF inputs from urban and industrial developments neighboring the study area. They also concluded that sediment was a continuing source for bioaccumulation rather than dioxins being removed by sediment burial.

This paper quantifies current dioxin levels in tissue and sediment at 45 locations in the HSC resulting in an extensive, one of its kind, dioxin dataset. The congener data are analyzed spatially to establish trends. Detailed fingerprint analyses are undertaken to understand the relationships, if any, between the observed concentrations in sediment, catfish, and crabs. Also, and because of an existing seafood advisory for the HSC and Upper Galveston Bay, there are data from the 1990s for tissue and sediment that allow examination of temporal changes in dioxin concentrations. This is important for two main reasons: (1) to evaluate if dioxin concentrations in the various media have declined as a result of reductions in discharges from the pulp and paper mill industry, and (2) to understand whether the dioxin concentrations in the channel reflect purely historical or legacy sources or possible continued releases from various industrial and municipal activities along the channel.

MATERIALS AND METHODS

Sampling locations

A total of 45 locations distributed along 15 water quality stream segments were sampled for dioxins in sediment, catfish, and crab tissue (Fig. 1). Sampling was undertaken between July 26 and September 11, 2002.

Sediment sampling

Sediment samples were collected with a stainless steel Ponar dredge. Prior to collection at each sample site, the dredge, stainless steel spoon, and polyethylene or stainless steel tray were rinsed with deionized water, then ambient water. Samples were collected and deposited into a stainless steel bowl. A minimum of three grab samples were composited using only the top 5 cm of sediment, mixed thoroughly with a clean stainless steel spoon, and deposited into a labeled, precleaned amber glass jar with a Teflon® seal. Sediment samples were preserved at 4°C or less prior to analysis.

Tissue sampling

Catfish tissue was harvested at selected sites based on the following selection order: hardhead catfish (*Arius felis*), blue catfish (*Ictalurus furcatus*), gafftopsail catfish (*Bagre marinus*), and channel catfish (*Ictalurus punctatus*). Gill nets or a fishing line with bait (shrimp or chicken) were used to catch enough catfish to obtain 50–100 g of muscle tissue. A minimum of three catfish were collected from each selected sample site to give a representative sample. Hardhead catfish with a total length of 300 mm was the target length for collection. Typically, blue catfish were collected in the upper stations and tributaries (probably due to greater presence of freshwater), while hardhead catfish were collected in lower reaches, side bays, and the HSC main stem (more presence of saltwater). Crab tissue was collected from blue crabs (*Callinectes sapidus*) using standard plastic coated wire mesh crab traps. A minimum of three blue crabs, and typically five to seven, were collected from each selected sample site to obtain the needed 50–100 g of muscle tissue. Blue crabs with a carapace width of 125 mm and greater were targeted.

Analytical methods

PCDD/PCDFs in sediment and tissue samples were quantified by high-resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) using EPA Method 1613B at a commercial laboratory. Sediment samples were homogenized, spiked with 15 $^{13}C_{12}$-labeled PCDD/PCDF internal standards and extracted using Soxhlet extraction apparatus. Tissue samples were homogenized, mixed with sodium sulphate until free flowing, and spiked with 15 $^{13}C_{12}$-labeled PCDD/PCDF internal standards, and mixed with sodium sulfate. Subsequently, the samples were extracted for 18–24 h using methylene chloride: hexane (1:1) in a Soxhlet extractor. The extract was evaporated to 10 mL, with 9 mL loaded on the GPC and 1 mL taken for lipid determination. The GPC extracts were then concentrated to ap-

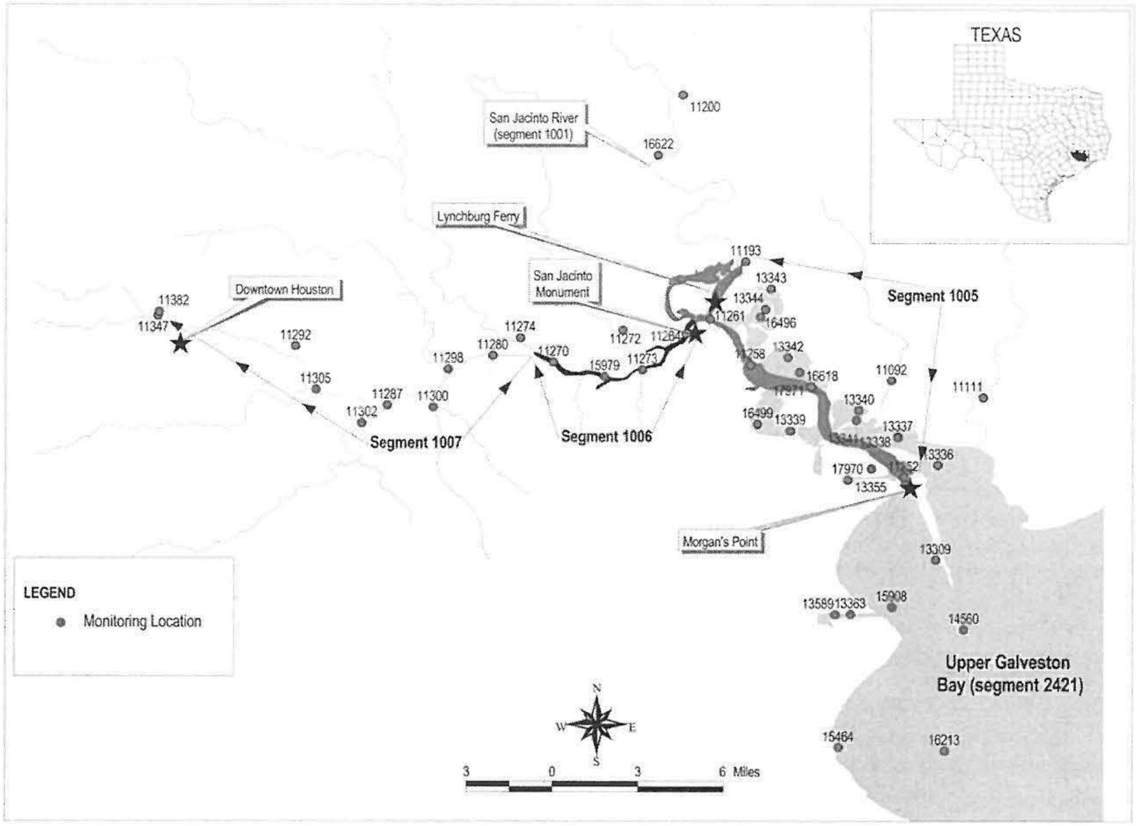


Figure 1. The Houston ship channel and upper Galveston Bay.

proximately 1 mL, ready for cleanup. The extracts (for both sediment and tissue samples) were then spiked with $^{37}Cl_4$–labeled 2378-TCDD enrichment efficiency standard and subjected to acid/base washes, multilayer silica, alumina, and carbon column cleanup procedures to remove interferences from the extracts. After cleanup, the extracts were concentrated to near dryness and spiked with recovery standards ($^{13}C_{12}$-1234-TCDD and $^{13}C_{12}$-123789-HxCDD) immediately prior to injection. Chromatographic separation was achieved with a DB-5 capillary chromatography column (60 m, 0.25 mm i.d., 0.25-μm film thickness). A second column DB-225 (30 m, 0.25 mm i.d., 0.25-μm film thickness) was used for confirmation of TCDF identification.

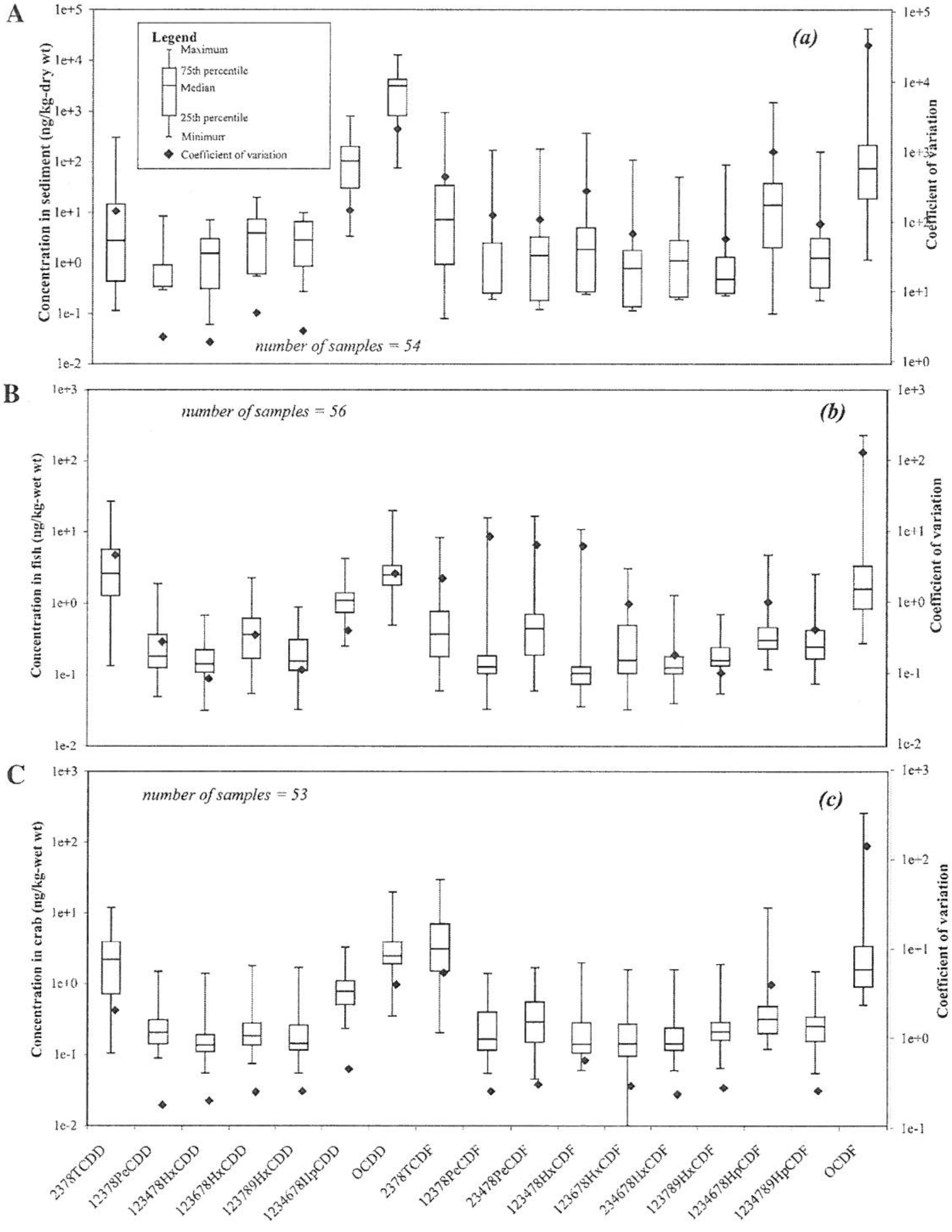
Quality control

Field duplicates and blanks were collected at a frequency of 5% or higher with each set of samples and processed in an identical manner to the samples. In addition, laboratory duplicates and blanks were run at a frequency of 5%. When detected, both field and laboratory blanks showed PCDD/PCDF levels below 5% of the levels in the samples. Results obtained from the duplicate samples were consistent and in agreement with the method requirements for the different congeners. Whenever a 2378-substituted congener was not detected, its concentration was assumed to be half of the detection limit for purposes of calculating total concentrations. Recoveries for 2378-substituted congeners ranged from 51 to 125% with an average of 89%. World Health Organization equivalence factors (TEFs) (Van den Berg *et al.*, 1998) were used to calculate TEQs.

RESULTS AND DISCUSSION

Sediment concentrations

Dioxin levels in sediment ranged from 0.1 to 443.8 ng TEQ/kg dry wt, with an average TEQ value of 37.2 ng/kg dry wt. Because the distribution is left-skewed, the median is a better measure of central tendency. In this case, the median was equal to 9.7 ng/kg dry wt. The concentrations of total PCDD/PCDF were not significantly correlated with total organic carbon content (TOC) in sediment ($p > 0.05$). Figure 2 shows the concentration distribution for the 2378-substituted dioxin congeners in sediment. The concentrations for the individual con-



Non-detects assumed as 1/2MDL

Figure 2. Concentration distribution of dioxin-like congeners in (**a**) sediment, (**b**) catfish, and (**c**) crab.

geners ranged from 0.1 to 42,000 ng/kg dry wt. Overall, sediment samples exhibited congener concentrations that followed the sequence OCDD > HpCDD > OCDF > HpCDF > TCDF > TCDD. Most of the total dioxin concentration can be attributed to OCDD with an average contribution of 85% when the individual congeners are summed. However, 2378-TCDD was the major contributor to the total TEQ (34% on average).

Tissue concentrations

Dioxin results for tissue show concentrations between 0.4 and 41.0 ng TEQ/kg wet wt for catfish and between 0.4 and 16.0 ng TEQ/kg wet wt for crabs, with average values of 5.1 and 3.8 ng TEQ/kg wet wt and median values of 3.4 and 3.7 ng/kg-wet wt, respectively. Lipid-normalized concentrations (catfish samples normalized to 3% lipids and crab samples to 2% lipids) yielded median TEQ values of 8.4 and 10.5 ng/kg wet wt for catfish and crab, respectively. It is noted that the health-based standard of 0.7 ng/kg (EPA criterion for a risk level of 10^{-5}) was exceeded in 94% of the catfish samples and in 90% of the crab samples. The concentrations of total PCDD/PCDF were not significantly correlated with lipid content ($p > 0.05$); correlation between 2378-TCDD and lipid content was significant for catfish even though the fit was weak ($r^2 = 0.32$). Relationships between dioxin concentrations and size and weight of the individual were also investigated but no statistically significant catfish or crab correlations were found.

Figure 2 shows the concentration distribution for the 2378-substituted congeners in the catfish and crab samples. The concentrations for the individual dioxin congeners ranged from 0.03 to 230.0 ng/kg wet wt for catfish and from 0.1 to 260.0 ng/kg wet wt for crabs. Most of the dioxin concentration in catfish can be attributed to OCDF with an average contribution of 20% to the total PCDD/PCDF sum (only the 2378-substituted congeners), while 2378-TCDF was the major contributor (23% on average) to dioxin concentrations in crabs. In both cases, 2378-TCDD was the major contributor to the total TEQ (average contribution of 74 and 65% for catfish and crab, respectively).

An important observation was the absence of high concentrations of OCDD in tissue relative to the remaining 16 congeners in contrast with what was observed in sediment samples (OCDD concentrations up to three orders of magnitude higher than those for the remaining congeners). In addition, sediment and tissue concentrations differed in the attenuation of variability (see coefficient of variation on the secondary y-axis for the different media in Fig. 2). Coefficients of variation were much lower in tissue (particularly crabs) than those for sediment.

Spatial trends

Sediment, catfish, and crab dioxin concentrations along the main channel are shown in Fig. 3. Segment 1006, a highly industrialized part of the channel, exhibited the highest average TEQ concentration in sediment and catfish, whereas segment 1005 showed the highest concentrations in crabs. While most main channel sediment concentrations were relatively low, TEQ concentrations for the San Jacinto River (segment 1001) and two of the tributaries were notable exceptions as was station 15979 in segment 1006 (peak TEQ in Fig. 3a), having concentrations greater than 100 ng TEQ/kg. Overall, catfish TEQ concentrations were lower in the side bays than in the main channel at the confluence with the bays (Segment 1005). TEQ concentrations in crab (Fig. 3c) also exhibited higher levels for main channel locations than those in side bays. Data in Fig. 3 also suggest that spatial variability is attenuated between sediment and tissue samples. Possible explanations include biota mobility and preferential bioaccumulation of lower chlorinated congeners.

Temporal trends

Dioxin concentrations in sediment and tissue collected in this study were compared to data gathered by others between 1989 and 2001. During the 1989–2001 time period, a total of 43 sediment samples (from 17 locations) and 133 tissue samples (from 19 locations) were collected and analyzed using method EPA 1613.

Sediment concentrations from this study were compared to concentrations measured in 1993, 1994, and 2001. It is noted, however, that differences in sampling and analytical methods used in the 1993–1994 study may limit the results of this comparison.

The average TEQ concentration in sediment from previous studies of 37.3 ng/kg dry wt is very similar to the average TEQ measured in this study of 37.2 ng/kg dry wt. Figure 4a shows a comparison of total TEQ concentrations in sediment from previous studies and data from this study. Overall, 2002 sediment TEQs in segments 1006 and 1001 (San Jacinto River) were higher than the values measured in previous studies, whereas concentrations in segments 1007 and 1005 were lower.

Due to the dioxin fish advisory in the channel, dioxin in tissue had been measured seven times between 1989 and 2001. In addition, two locations in the channel that are downstream of former paper mill discharges (near the San Jacinto Monument and the Lynchburg Ferry; Fig. 1) had been monitored annually from 1992 to 2001. Historically, the highest TEQ for both catfish and crab was measured near the San Jacinto Monument, the intersection between segments 1001, 1005, and 1006. The lev-

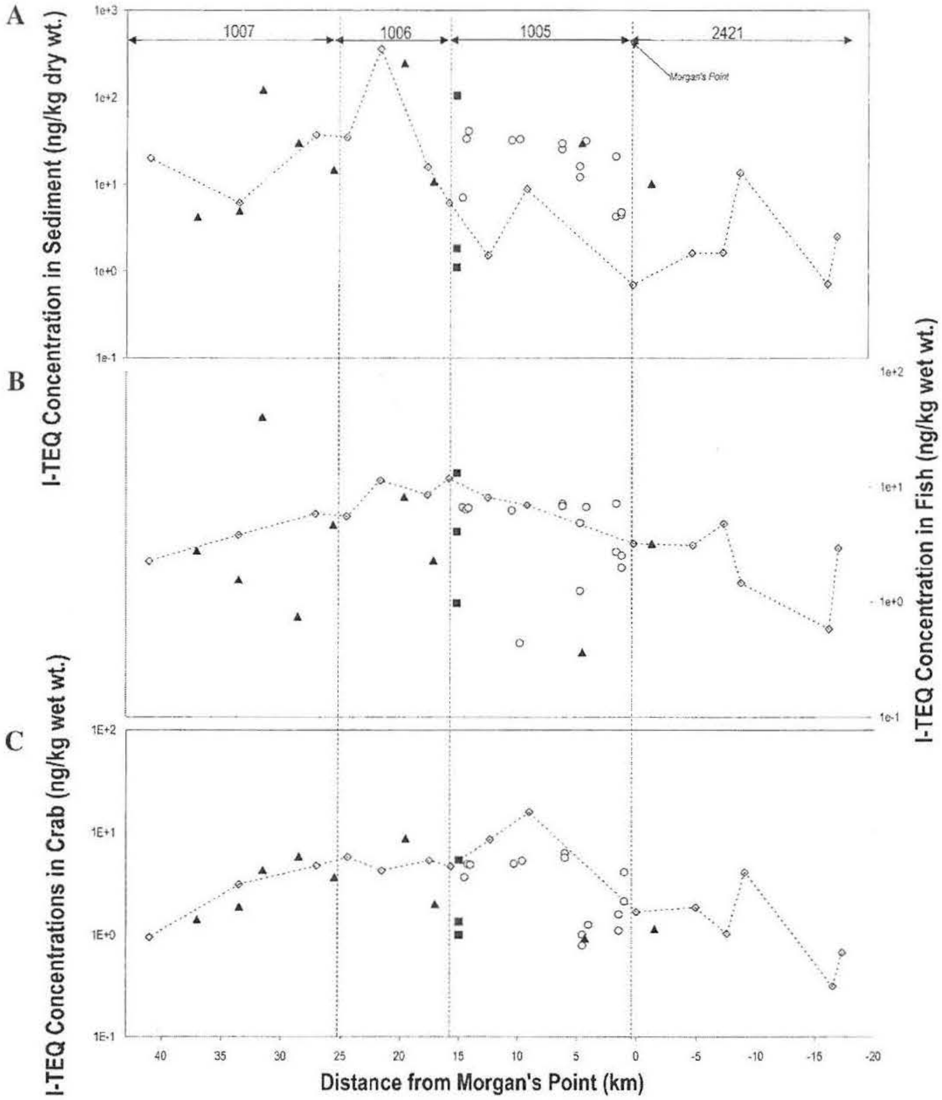


Figure 3. Total TEQ concentration profiles in the main channel in (**a**) sediment, (**b**) catfish, and (**c**) crab in the main channel (◇), San Jacinto River (■), side bays (○), and main tributaries (▲).

els of dioxins measured in tissue samples in this study are compared to their historical counterparts in Fig. 4b and c. The data in Fig. 4b and c were not lipid-normalized as information on percent lipids was not available from past studies. The decision not to lipid-normalize the data is also supported by the lack of correlation between lipid content and dioxin concentrations. TEQ levels in catfish measured in 2002 appear to be higher than those measured previously with the exception of stations 11252 and 13337 (Fig. 4b). The mean of the total TEQ (using data for the stations measured both in previous studies and in this study) was found to be 8.6 and 5.5 ng/kg wet wt for the previous and current studies, respectively. In contrast, concentrations in crabs from previous studies appear to be higher than those measured in this study with the exception of station 11273 (Fig. 4c). The average TEQ in crabs from previous and current studies were 3.7 and 3.9 ng/kg wet wt, respectively.

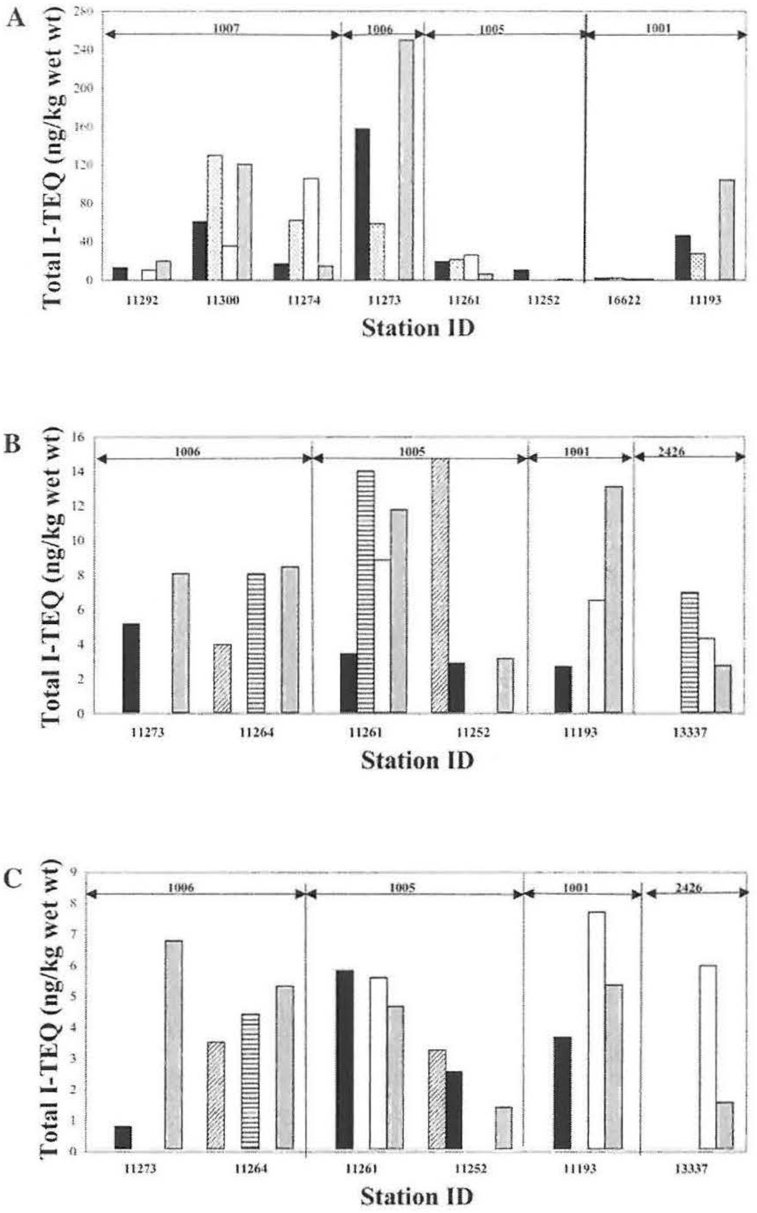


Figure 4. Comparison of past and current I-TEQ levels in (**a**) sediment, (**b**) catfish, and (**c**) crab by year [1990 (▨), 1993 (■), 1994 (▦), 1996 (⊟), 2001 (□), and 2002 (▣)].

Figure 5 shows an analysis of temporal trends for each of the dioxin congeners in catfish at a location near the San Jacinto Monument (location showing the highest concentration in catfish). This analysis was conducted using the data collected from 1992 and including the current study. Overall, PCDDs were higher than PCDFs with 2378-TCDD showing the highest levels throughout the entire period. It can be seen from Fig. 5 that the PCDD lines remain relatively parallel from 1992 to 2002, with the exception of 123678-HxCDD, which did not follow the trend

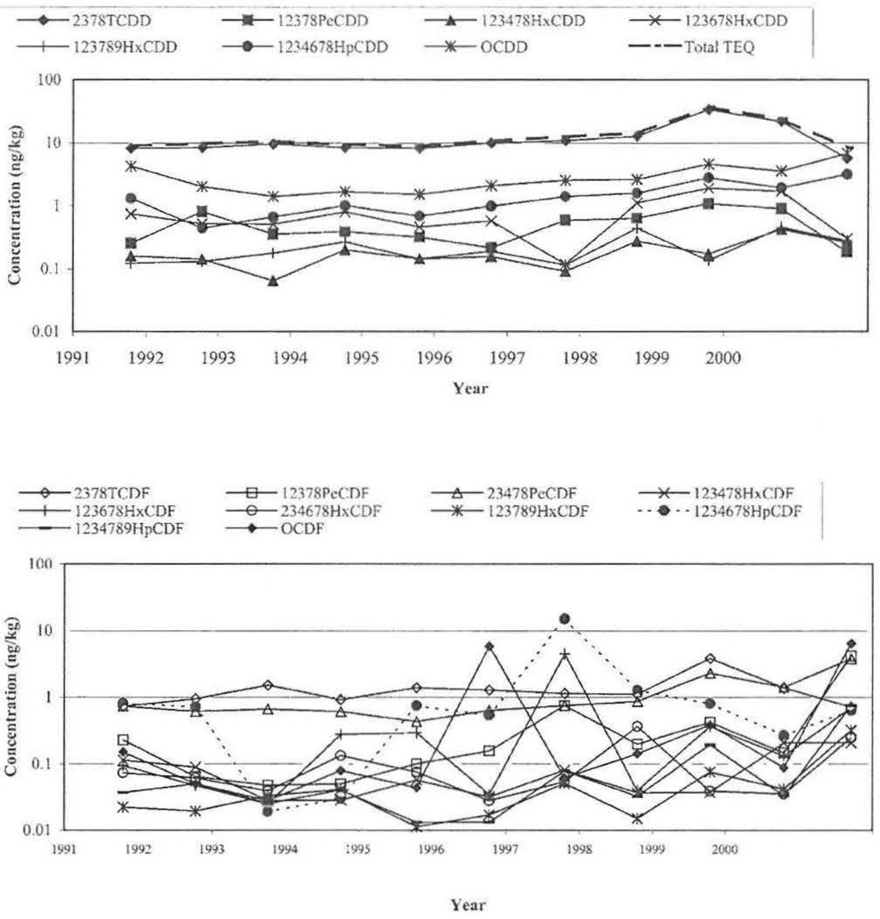


Figure 5. Time series of dioxin concentrations in catfish at San Jacinto monument.

in 1997. In contrast, the PCDF lines did not follow the same trends, especially those for congeners 12378-PeCDF, 123678-HxCDF, 234678-HxCDF, 1234678-HpCDF, and OCDF, which differ substantially from the remaining curves after 1995. This may suggest a change in dioxin sources around 1995. Data in Fig. 5 also indicate that, in general, there has been little change in congener concentrations with time. Linear regressions for each of the curves showed that, for most of the congeners the slope of the best-fit line was not significantly different from zero. The only exceptions were the congeners 2378-TCDD, 123478-HxCDD, 123789-HxCDF, and 1234789-HpCDF, which exhibited a slightly increasing trend with time (p-values between 0.01 and 0.05 and r^2 between 0.3 and 0.5). Results from a Mann-Kendall test for this data set confirmed the results from the linear regressions. The total TEQ showed an increasing trend with time (p-value = 0.05).

Fingerprint analysis

Comparison of the patterns of PCCD/PCDFs in the three media using 2002 data is shown in Fig. 6. Six stations were selected for this purpose: three "contaminated" stations (15979, 11193, and 11264), that are locations with TEQ concentrations in all media among the 10 highest; and three "background" stations, which are locations with either TEQ concentrations in all media among the 10 lowest (11200 and 16213) or located in a segment with no point source discharges (13340). This comparison provides information on the type of sources affecting the various locations. Even though sediment data from the six selected sites show a clear dioxin signature (PCDD > PCDF), differences between contaminated and background sites were observed (Fig. 6a). For the samples near the more industrialized area (15979 and 11264 in

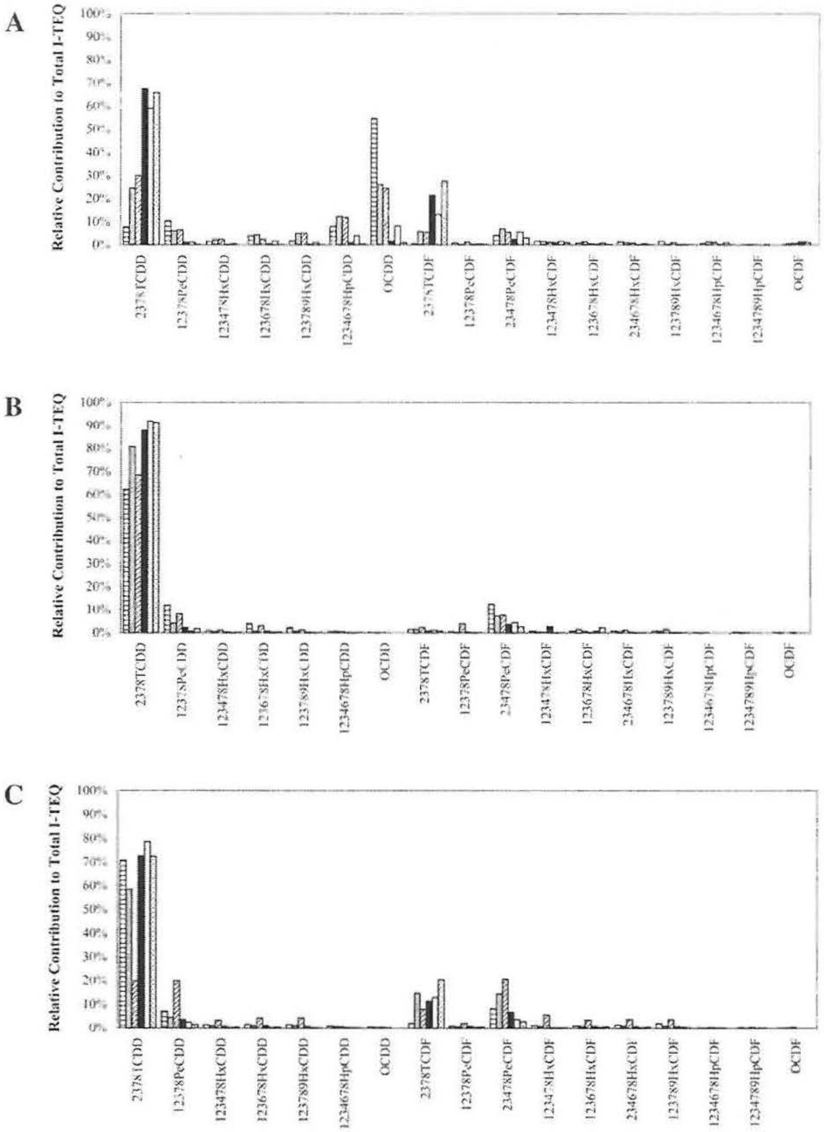


Figure 6. Relative individual contribution to total I-TEQ for background sites [11200 (⊟), 13340 (▤), 16213 (▨)] and contaminated sites [15979 (■), 11264 (□), 11193 (▦)].

segment 1006 and 11193 in segment 1001), 2378-TCDD contributes more than 60% to the total TEQ, while for background sites (11200, 16213, and 13340), 12378-PeCDD is an important contributor to the total TEQ along with 2378-TCDD. It is also noted that 2378-TCDF contributes about 20% of the total TEQ in the contaminated sites, while its contribution in background locations is between 0.8 and 7% only.

Congener fingerprints for catfish samples collected in this study (Fig. 6b) are similar for all locations with an almost exclusive contribution of 2378-TCDD to the total TEQ (>70%). 12378-PeCDD and PeCDFs contribute about 25% to the total TEQ for the background sites, while those congeners make up only about 6% of the total TEQ in contaminated sites. It is noted that the dioxin signatures observed in catfish samples differ from those for sediment, mainly in the absence of higher chlorinated PCDDs present in sediment (Fig. 6). Other researchers have reported differences between the patterns of sediment and fish samples collected from the same areas (Sakurai *et al.,* 1996; Bonn, 1998; Yunker *et al.,* 2002). Possible reasons include the preferential bioaccumulation of the lower chlorinated congeners over the others, increased potential for accumulation of the higher chlorinated congeners in organic matter (greater K_{oc} values), and food chain effects.

While 2378-TCDD is the major contributor to total TEQ in most crab samples, dioxin fingerprints for crab samples (Fig. 6c) show differences between background and contaminated sites. 12378-PeCDD and 23478-PeCDF seem to be somewhat important in background locations, whereas at contaminated sites, 2378-TCDF is the major additional contributor to TEQ. Station 16213 varies considerably from the other background locations with the highest contribution from 12378-PeCDD and lower contributions from 2378-TCDD and 23478-PeCDF to the total TEQ.

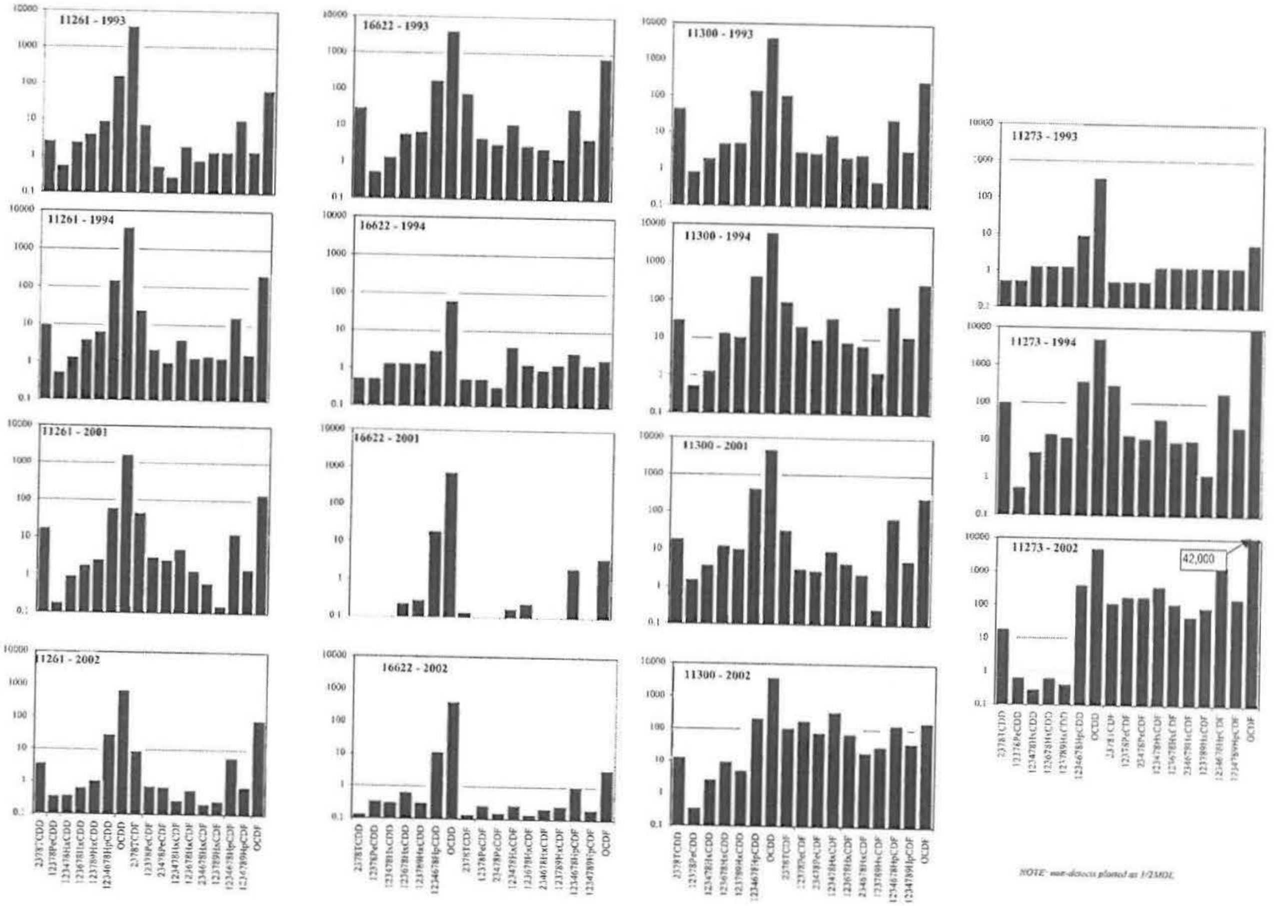
Changes in dioxin fingerprints over time were evaluated to determine any resulting changes in patterns due to modifications in regulated industrial processes. Figure 7 shows the congener profiles in sediment samples at locations sampled during at least three events. It can be seen that, in general, sediment samples have exhibited the same patterns over time. The only station that showed a change in pattern was 11300, for which recent data showed higher concentrations of furans. Station 16622 exhibits a somewhat consistent pattern over time with high concentrations of the hepta/octa dioxins and furans; however, concentrations of 2378-TCDD and 2378-TCDF seem to have decreased over time. It is also noted that the dioxin signature for station 11273 (Patrick Bayou, a tributary to the HSC) differs significantly from other stations (samples collected in 1994 and in this study) and shows high concentrations of OCDF after 1993. This may indicate that the sources present in Patrick Bayou are different from the ones at the other locations. An OCDF dominated profile was observed by Evers *et al.,* (1993) in sediments from the North Sea, and was linked to industrial operation discharges related to the production of chloroaliphatic compounds and a chloralkali plant in the area.

A similar analysis for tissue showed that catfish and crab fingerprints have not changed dramatically over time. Catfish samples have consistently exhibited high concentrations of 2378-TCDD and OCDD, while crab samples showed a decreasing presence of the PCDFs. The only exception again was observed for station 11273 (Patrick Bayou) that showed much higher levels of 2378-TCDF and OCDF in 2002 than in 1993.

The congener profiles in sediment for three of the locations (11261, 16622, and 11300) are similar in that the OCDD concentration in each sample is much higher than any of the other congeners. This type of profile is similar to those reported for sediments from the Great Lakes (Czuczwa and Hites, 1984) and from the Willamette Basin (Bonn, 1998). Eitzer and Hites (1989a, 1989b) and Koester and Hites (1992a, 1992b) suggested that this observed behavior might be the result of the atmospheric transformations (atmospheric transformations tend to enrich the D8 homolog). Thus, the results from this study suggest that nonpoint atmospheric sources may be a significant contributor of TEQ to the sediment in the HSC. It is, however, unlikely that atmospheric deposition is the only source acting at these sites. Other possible sources associated with such a profile include technical grade pentachorophenol (Hagenmaier and Brunner, 1987), sewage sludge (Hortsmann and McLachlan, 1995), diesel emissions, coal combustion, black-liquor recovery furnace flue gas (Palazzolo *et al.,* 1987), scrap wire, and scrap car incineration (van Wijnen *et al.,* 1992) and chimney soot from oil central heating (Thoma, 1988). Data from this study indicate that the only stations that show a somewhat different congener pattern for sediment samples (where OCDF concentrations are at or above the level of OCDD concentrations) are 11273 and 15979 (fingerprints not shown for the latter). These two stations are located in one of the most contaminated segments and the difference in fingerprints may be indicative of the presence of additional and/or different sources of dioxin.

To further explore the differences in dioxin signatures exhibited by the sediment samples, principal component analysis (PCA) was used. Individual 2378-substituted congener data were normalized by the total concentration of PCDD/PCDF in each sample to minimize any statistical bias caused by the difference in the order of magnitude of the concentrations. Two factors were extracted from the analysis accounting for 98.9% of the total variance. Figure 8 presents a principal component score plot of the two main components using all the 45 sediment stations (plus duplicates when collected). The scatter plot of the component scores showed evident differences in the signatures of the samples collected at locations 11273, 15979, 11300, and 11193. These four stations seem to be affected by a different combination of sources/processes. The remaining samples appear to cluster in the left-top quadrant of the plot with the exception of stations in segment 1007 and a few samples from Upper Galveston Bay (segment 2421) that presented negative values for PC2. This cluster is mainly dominated by high concentrations of OCDD.

Finally, to further analyze if the patterns of contamination found in this study were similar to those observed



NOTE: non-detects plotted as 1/2MDL

Figure 7. Concentrations (ng/kg dry wt) of the 2378-chlorine substituted PCDD/PCDFs in sediment samples at selected locations.

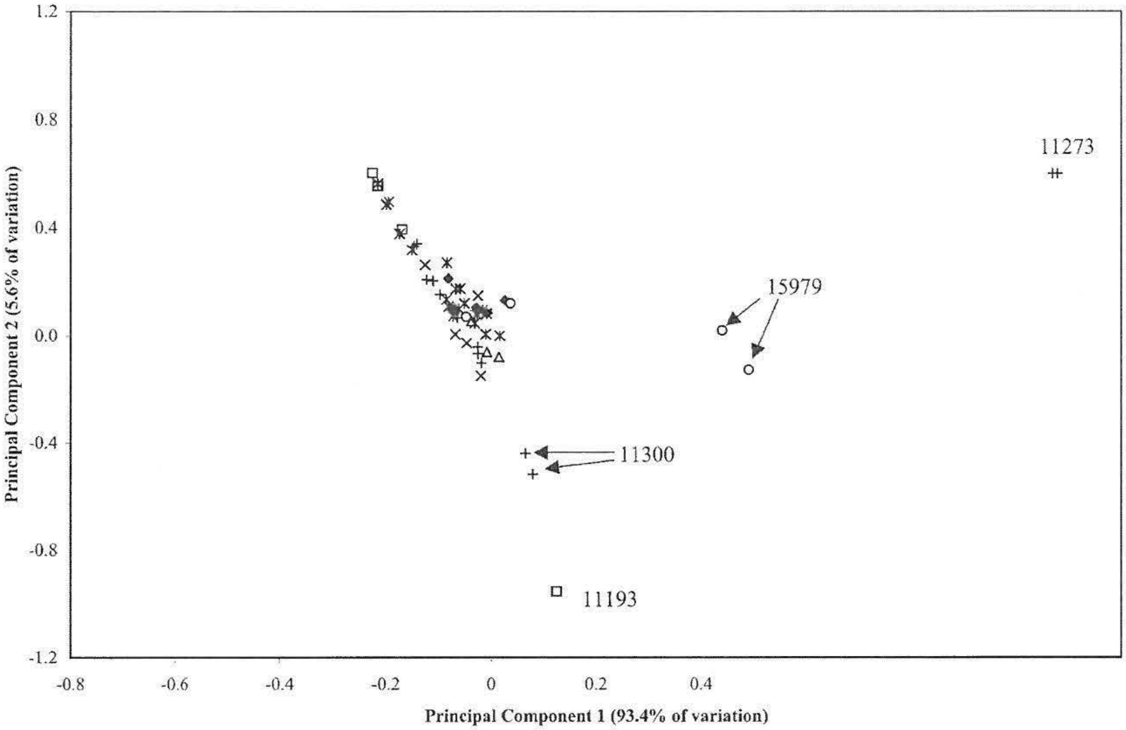


Figure 8. Plot of the two principal components for all sediment samples. Locations in segments 1001 (□), 1005 (◆), 1006 (○), 1007 (△), 2421 (×), and side bays (*).

from past data, the relationship between the sum of 2378-substituted PCDDs and 2378-substituted PCDFs was plotted for sediment, catfish, and crab samples (Fig. 9). Data in Fig. 9 indicate that for sediment samples, the concentration patterns seem equivalent, with slightly different ΣPCDD/ΣPCDF average ratios indicated by the regression line. Tissue data, on the other hand, exhibited different ratios for the current dioxin data with a considerable increase in PCDF contribution, due mainly to relatively high concentrations of OCDF measured in the current study. This may suggest that there are current sources enriched with the higher chlorinated dibenzofurans that are affecting water concentrations that are then adsorbed/ingested by catfish and crabs.

CONCLUSIONS

Nearly all 2378-substituted PCDD/PCDF compounds were detected in all sediment and tissue samples collected from 45 locations in the Houston Ship Channel in Texas. Sediment total dioxin concentrations exhibited high OCDDs while catfish and crab concentrations were dominated by OCDFs and TCDFs, respectively. More than 90% of the catfish and tissue samples analyzed in this study exceeded the health-based standard of 0.7 ng /kg (EPA criterion for a risk level of 10^{-5}). Comparison between the data from this study and earlier dioxin measurements made in the 1990s suggest that despite regulatory controls on discharges from pulp and paper mills, there has been little change over time in dioxin concentrations in sediment and tissue from the HSC. Ongoing PCDD/PCDF inputs from urban and industrial areas along the channel may provide a partial explanation for the lack of change. Stations located in the industrialized channel showed consistently high dioxin levels among the three sampled media. The lack of a decreasing trend may also be the result of sediment transport dynamics, redistribution of historic sediments by tidal currents, erosion in previously depositional environments, and dredging/disposal practices. Ongoing studies are exploring these possible reasons. Analysis of sediment fingerprints suggests that atmospheric nonpoint sources may also be a major contributor to sediment dioxin contamination in the study area. Catfish and crab fingerprint

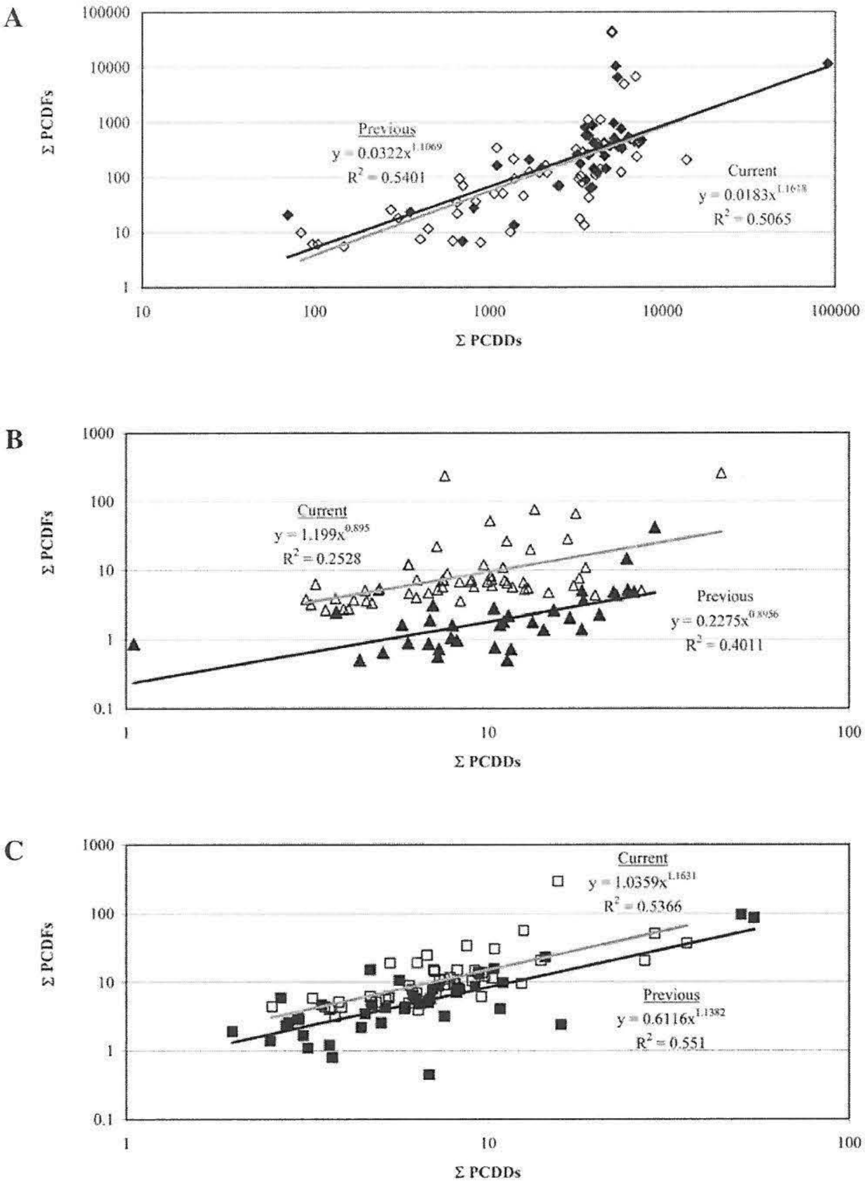


Figure 9. Relationship between PCDDs and PCDFs for past (closed symbols) and current (open symbols) data for (**a**) sediment, (**b**) catfish, and (**c**) crab.

analyses, on the other hand, suggest the presence of active sources of dioxin to the HSC that are altering the dissolved concentrations in water, and subsequently reach the biota through adsorption rather than ingestion.

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