

**NOAA National Status and Trends Program: PCDD/PCDF  
Concentrations in Bivalves and Sediments****Terry L. Wade, Piero R. Gardinali, Thomas J. Jackson, Jose L. Sericano and  
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833 Graham Rd. College Station, TX. 77845**Abstract**

As part of the National Oceanic and Atmospheric Administration (NOAA), National Status and Trends (NS&T) Mussel Watch Program, 55 bivalves and 7 sediment samples were analyzed for 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD and PCDF). Bivalve samples were collected from selected U.S.A. East, Gulf and West coast sites, while the sediment samples were all from the Gulf coast. Sediment concentrations for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin and dibenzofuran (TCDD and TCDF) ranged from 0.35 to 2.6 pg/g and 0.42 to 9.1 pg/g, respectively. The 2,3,7,8-TCDD and 2,3,7,8-TCDF represent only a small percentage of the total PCDD and PCDF in the sediments. The concentration of TCDD and TCDF in bivalves ranged from not detected (ND) to 25 pg/g and ND to 140 pg/g, respectively. In contrast to the sediment samples, most bivalve samples contained low proportions of the higher molecular weight PCDDs and PCDFs. The relative toxicological importance of 2,3,7,8-substituted PCDD/PCDF to the bivalves based on toxicity equivalency factors is provided.

**Introduction**

Over the last several decades problems associated with the chemical contamination of the marine environment have received increasing attention. Numerous studies have been undertaken to identify the sources, transport, and effects of a variety of elements and compounds. Particular attention has focused on the coastal zones and estuaries especially near large population centers. These areas experience the largest potential impact from chemical contamination and may be the most sensitive to the accumulation of toxic compounds. Professor Edward Goldberg in 1975 outlined a global scale environmental monitoring program based on the sentinel organism concept to detecting trends in concentrations of several important marine contaminants in coastal marine waters<sup>(1)</sup>. Mussels and other bivalve species would be used as sentinel organisms because they are sedentary and they have the ability to bioconcentrate the pollutants of interest.

In the United States, the "Mussel Watch" Program was initiated by the U.S. Environmental Protection Administration (EPA) in the mid-1970's and became an operational contaminant monitoring program directed by the U.S. NOAA as a part of the National Status and Trends (NS&T) Program in 1985. The NOAA program

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now has 11 years of bivalve contaminant data. The overall goal of the "Mussel Watch" program is to assess and document the status and long-term changes in the environmental quality of coastal and estuarine environments. In order to meet this goal, a series of systematic observations of selected chemical contaminants (e.g., trace metals, butyltins, PAHs, PCBs and pesticides) in representative samples of bivalves are undertaken. The project is intended to provide information based on systematic observations of the environmental quality of the nation's coastal and estuarine regions so that decisions on the use and allocation of these resources may be reliably and accurately made.

The NS&T program maintained the flexibility to add additional analytes of concern to the program as these contaminants were identified. One example was the addition in 1987 of butyltins, a component of anti fouling paints. Recently other analytes of potential concern have also been added. In 1995 selected bivalves and sediment samples were analyzed for 2,3,7,8-substituted polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD and PCDF). The objectives of this research was to determine the geographic distribution of these contaminants in mussels at selected near coastal sites, locate "hot spots" or "problem" areas, and determine if broad areas of selected regions are contaminated. The toxicity equivalency factor approach will also be employed to assess the relative toxicity of PCDDs and PCDFs. The concentrations of PCDD and PCDF in sediment and bivalves from the same collection sites are compared.

## Methods

Bivalve oyster or mussel samples (*Crassostrea virginica*, *Mytilus edulis*, *Mytilus californianus*) were collected either by hand or dredging. The bivalves were scrubbed to remove as much mud and debris as practical with water from the collection site and a pure bristle brush. Twenty or more bivalves were triple wrapped in combusted aluminum foil, then double bagged in labeled Ziplock bags. The samples were then returned to the laboratory on ice. In the laboratory the bivalves were unwrapped, the shells washed with water, opened and the soft tissue placed in a glass jar with a teflon lined screw cap and frozen until they were analyzed.

Sediment samples (100 g or more) were collected by hand with a teflon scoop in shallow water or with a Young modified Van Veen grab sampler. Sampling gear was cleaned just prior to use with methanol and rinsed with water from the sampling site. The top 1-2 cm of sediment was collected. The sediment was placed in a glass jar with a teflon lined screw cap and returned to the laboratory on ice. Sediment samples are stored frozen in the laboratory until they were extracted.

The QA/QC procedures included analysis of matrix spikes, duplicates and laboratory blanks with each batch of samples. In addition a marine reference sediment, SRM 1941a from the National Institute of Standards and Technology (NIST) was analyzed with each batch of samples. For tissue samples either reference tissues, EDF-2526 from Cambridge Isotopes Laboratory or Carp-1 from National Research Council of Canada (NRC) were analyzed with each sample batch. The sediment SRM does not currently have certified PCDD/PCDF concentrations. However, previous analyses of this SRM have proven its value as a homogeneous estuarine reference sediment (collected from Baltimore Harbor) that contains PCDD/PCDF(2).

The method used for PCDD/PCDF sediment and tissue analyses has been reported(2,3,4). The method was developed to determine the concentrations of 7 PCDD and 10 PCDF isomers having chlorine substitution in the 2,3,7,8 positions. Tissues (1 to 3 g dry weight) were spiked with appropriate internal standards, mixed with sodium sulfate and extracted with methylene chloride (100ml) three times using a Tekmar tissumizer for 5 min. each time. Sediments (10 to 25 g dry weight) were spiked with the appropriate internal standards and were extracted for at least 24 hours with toluene in a soxhlet extractor fitted with a Dean-Stark water trap. PCDD/PCDF were separated from interfering compounds in sample extracts by mixed-bed silica, basic alumina, and AX-21 Super Activated Carbon column chromatography. The extracts were reduced to a final volume of 20  $\mu$ L and the appropriate recovery standards added.

Two  $\mu$ L of the concentrated extract were injected into an high resolution gas chromatography/high resolution mass spectrometry (HRGC/HRMS) system capable of performing selected ion monitoring at resolving powers of at least 10,000. The identification of the sixteen 2,3,7,8-substituted isomers for which a  $^{13}\text{C}$ -labeled standard is available was based on their elution order from a DB-5MS analytical column with the corresponding retention time and the simultaneous detection of the two most abundant ions in the molecular ion region. The identification of octachlorodibenzofuran (OCDF) was based on its retention time relative to  $^{13}\text{C}$ -OCDD. Confirmation of the level of chlorination was based on a comparison of the ratios of the integrated ion abundance of the molecular ion species to their theoretical abundance ratios. Quantification of the individual congeners was achieved with the establishment of a multipoint calibration curve for each analyte. Concentrations of 2,3,7,8-TCDF were confirmed on a DB-225 analytical column(4).

## Results and Discussion

Sediment concentrations for TCDD, TCDF, total PCDD (sum of 7 isomers) and total PCDF (sum of 10 isomers) ranged from 0.35 to 2.6 pg/g, 0.42 to 9.1 pg/g, 160 to 2900 pg/g and 22 to 402 pg/g, respectively. The concentration of TCDD, TCDF, total PCDD and total PCDF in bivalves ranged from not detected (ND) to 25 pg/g, ND to 140 pg/g, ND to 535 pg/g and ND to 140 pg/g, respectively. It should be noted that TCDD was detected in only a small fraction (25%) of the of the bivalves analyzed. A comparison of the sediment and bivalve distribution of the 2,3,7,8-dioxin and furan isomers for Galveston Bay, Todds Dump (GBTD) is shown in Figure 1. The oysters from this site contain only TCDF, TCDD, HpCDD and OCDD, while the sediments from this site contained all the target isomers with the exception of HxCDD. The 2,3,7,8-TCDD and 2,3,7,8-TCDF represent only a small percentage of the total PCDD and PCDF in the sediments but are the major isomers in the bivalve samples (Figure 1). This is likely the result of preferential accumulation of these lower molecular weight isomers. When mussels were transplanted from a relatively clean bay to a more highly contaminated one in Japan the concentrations of all the PCDD isomers rapidly increased(5), and reached concentrations one-half that of the indigenous mussels. However, TCDD concentration were nearly the same as those of the indigenous mussels, indicating preferential accumulation of TCDD. The range of TCDD and total PCDD concentrations for mussels from coastal areas of Japan ranged from 2.4 to 350 pg/g and 7.6 to 410 pg/g, respectively(5). The TCDD concentrations are higher than those reported here, while the range for total PCDD are similar.

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The relative toxicological importance of 2,3,7,8-substituted PCDD/PCDF to the bivalves from different locations can be compared based on toxicity equivalence factors (TEQ)<sup>(6)</sup>. The total TEQ (Figure 2) for the 55 bivalve samples ranged from ND to 40 pg/g dry weight of 2,3,7,8-TCDD equivalents. The frequency distribution for total TEQ (Figure 2) shows that 30% of the TEQ is below 1 pg/g and that the geometric mean is 2 pg/g. The sample with the highest TEQ (40 pg/g) was the GBTD oyster sample shown in Figure 1. The sample moisture content was 94% and therefore the TEQ on a wet weight basis is 3 pg/g wet weight 2,3,7,8-TCDD equivalents. A human health advisory would not be implemented based on these levels. However, these NS&T sites are selected to be removed from the influence of know point sources. There has been a human consumption advisory for fish from the Houston Ship Channel in Galveston Bay, that is up bay from the GBTD site and closer to the probable input source. It should also be noted that the TEQ of other dioxin-like compounds are (i.e. PCB) may add to this toxicity<sup>(7)</sup>.

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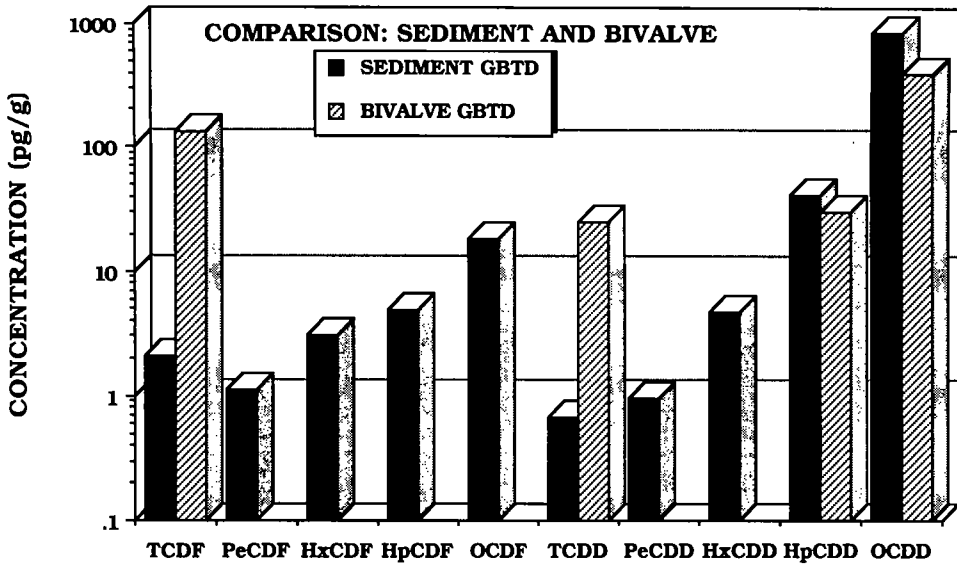


Figure 1. Isomer distribution of sediment and oysters from Galveston Bay

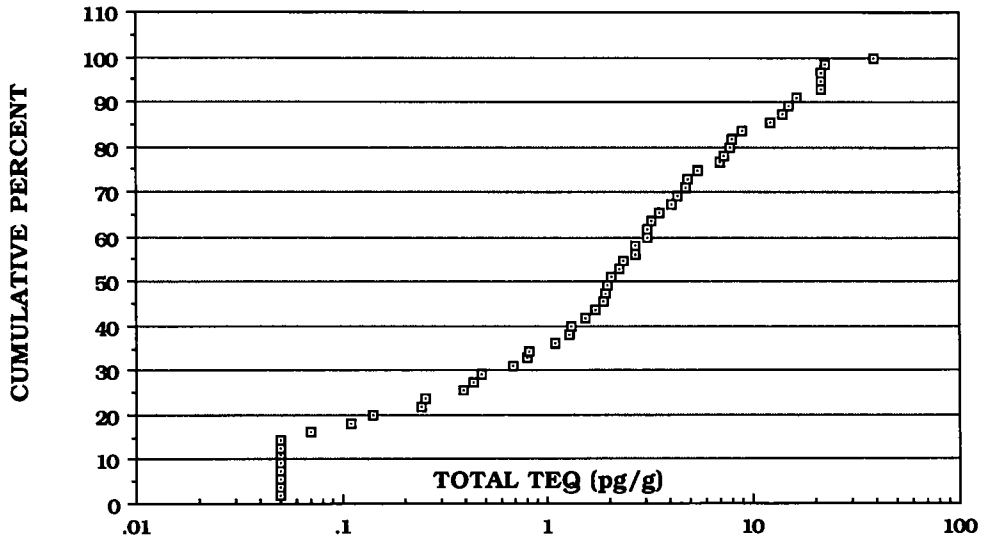


Figure 2. Total TEQ frequency distribution for 55 bivalve samples