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# A Major Incident of Dioxin Contamination: Sediments of New Jersey Estuaries[†]

**Richard F. Bopp,** [*,‡,§,∥] **Michael L. Gross,** [⊥] **Huayi Tong,** [⊥] **H. James Simpson,** [‡,§] **Stephen J. Monson,** [⊥] **Bruce L. Deck,** [‡,ℱ] **and Fredrika C. Moser** [+,ℐ]

Lamont-Doherty Geological Observatory of Columbia University, Palisades, New York 10964, Department of Geological Sciences, Columbia University, New York, New York 10027, Department of Chemistry, University of Nebraska, Lincoln, Nebraska 68588, and State of New Jersey Department of Environmental Protection, Division of Science and Research, Trenton, New Jersey 08625

■ 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD) was measured in sediments and suspended matter samples from estuaries adjacent to an industrial site in Newark, NJ, where chlorinated phenols had been produced. Present day and recent historical levels of 2,3,7,8-TCDD contamination were established through the use of radionuclide time tracers ($^7$Be, $^{137}$Cs). Concentrations up to 21 000 parts per trillion (ppt) were found in sediments deposited near the site. Pre-1950 production of DDT at the same industrial site provided another sensitive pollutant source tracer. The total deposition of 2,3,7,8-TCDD in Newark Bay sediments since the late 1940s has been approximately 4-8 kg, among the largest releases documented to date. Sediments dredged from estuaries in this region have been disposed of on land surrounding Newark Bay and at a coastal ocean dumpsite.

## Introduction

Polychlorinated dibenzo-*p*-dioxins (PCDDs) in the environment originate as byproducts of industrial chemical processes and via combustion. A major industrial source of PCDDs was the production of sodium 2,4,5-trichloro-

phenate, which was used in the synthesis of the herbicides based upon (2,4,5-trichlorophenoxy)acetic acid (2,4,5-T), major components of Agent Orange (*1*). Between approximately 1948 and 1969, a chemical manufacturing facility located in Newark, NJ, at 80 Lister Ave. on the west bank of the Passaic River (Figure 1) produced sodium 2,4,5-trichlorophenate, which was used on site to synthesize 2,4,5-T. Production capacity of 2,4,5-T at the plant averaged ~800 tons/year (*2, 3*), approximately 15% of the total U.S. output (*4*).

Although the manufacture of several additional chlorinated phenol products and a fire at the facility in 1960 led to a complex mixture of PCDDs found in soil from the site (*5*), a high relative abundance of a particular isomer, 2,3,7,8-TCDD, characteristic of sodium 2,4,5-trichlorophenate synthesis, was also found (*5*). On the basis of animal feeding studies, this compound is among the most toxic chemicals ever tested (*6*). At a level of ~2000 parts per billion (ppb), 2,3,7,8-TCDD comprised ~15% of the PCDDs in a surface soil sample from the site (*5*). In contrast, 2,3,7,8-TCDD is only a minor component of the PCDDs in incinerator gases and fly ash (*7, 8*) and in recent lake sediments and air samples (*9-11*).

In this paper, we examine the levels, geographical extent, and history of 2,3,7,8-TCDD contamination in sediments of estuaries influenced by runoff and discharges from the 80 Lister Ave. site. Time scales are established via measurements of natural and manmade radionuclides in sediment core sections (*12*). The distributions of related contaminants are also discussed. Octachlorodibenzo-*p*-dioxin (OCDD) was the most abundant congener in the 80 Lister Ave. soil sample (*5*) and is a major component of combustion-produced PCDDs (*7-9*). 2,3,7,8-Tetrachlorodibenzofuran (2,3,7,8-TCDF) is a highly toxic contaminant formed along with 2,3,7,8-TCDD during sodium

[†] Lamont-Doherty Geological Observatory Contribution No. 4747.
[‡] Lamont-Doherty Geological Observatory.
[§] Columbia University.
[∥] Current address: State of New York Department of Environmental Conservation, Albany, NY 12233.
[⊥] University of Nebraska.
[ℱ] Current address: Scripps Institution of Oceanography, University of California, San Diego, La Jolla, CA 92093.
[+] State of New Jersey Department of Environmental Protection.
[ℐ] Current address: Institute of Marine and Coastal Sciences, Rutgers, The State University of New Jersey, New Brunswick, NJ 08903.
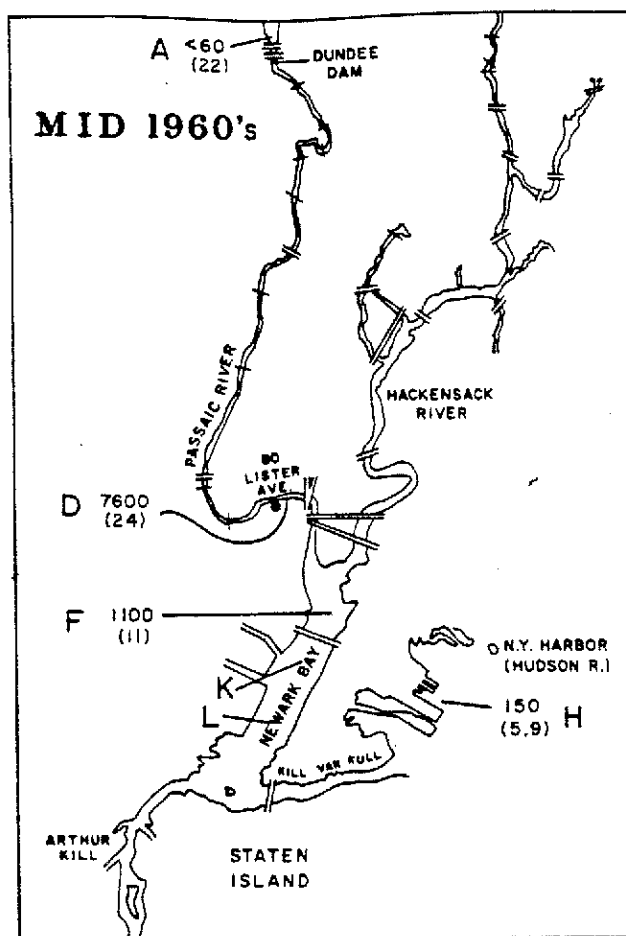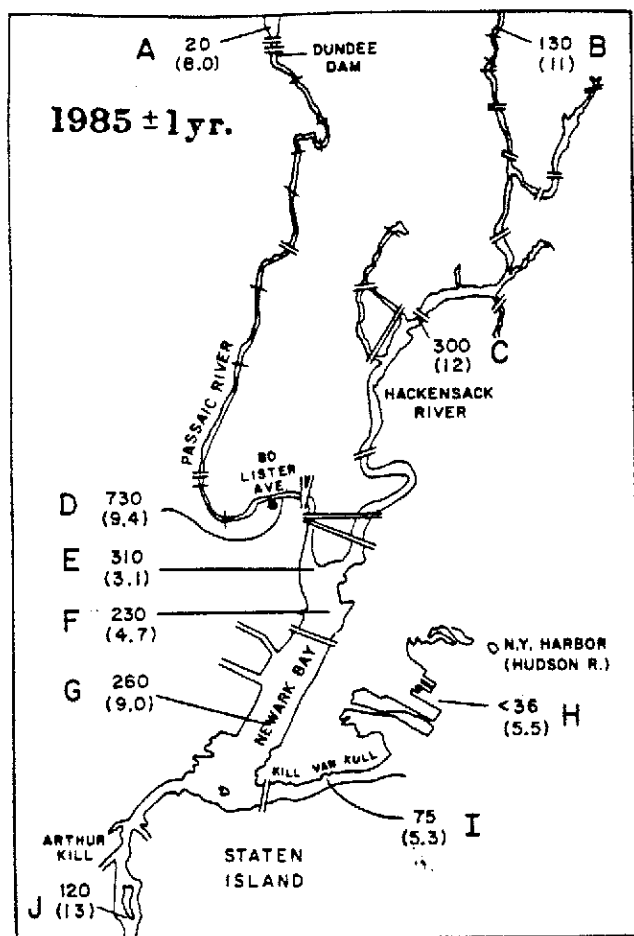
**Figure 1.** Maps of the study area showing 2,3,7,8-TCDD concentrations in parts per trillion on particles from two time horizons. OCDD concentrations in parts per billion are given in parentheses. Sampling sites are designated A–L. All data are from sediment core sections except at sites G and J, where data from suspended particle samples is reported.

2,4,5-trichlorophenate synthesis (1). p,p'-DDD is a major DDT-derived compound found in anaerobic sediments. DDT was synthesized at the 80 Lister Ave. plant between the early 1940s and 1959 (2, 3).

*Experimental Section*

Sediment samples were collected with gravity and piston corers. Gram-sized suspended particle samples were collected on precombusted, 25.4-cm-diameter quartz fiber filters (Whatman QMA) by using a large-volume, in situ pumping system (LVFS) (13). Core sections and filters were dried under a flow of air filtered through Florisil to minimize atmospheric contamination. Sediment cores are identified by a letter corresponding to the sampling site (Figure 1) followed by a number to distinguish multiple cores from the same site.

Chlorinated hydrocarbon analyses were performed on individual filters and subsamples of ground sediment core sections (ca. 1 g). Homogeneity of ground sediment samples was indicated by the reproducibility of chlorinated hydrocarbon results for replicate subsample analysis. In a similar study of Hudson River sediments, p,p'-DDD analysis of two separate portions of 14 sediment samples yielded an average coefficient of variation of 5.2% (14). PCDD and polychlorinated dibenzofuran analysis was based on GC–MS procedures employed at the University of Nebraska (15) and validated in several interlaboratory comparison studies (16–18). Acid treatment of samples prior to extraction (19) was found to improve recovery of the $^{13}C$-labeled internal standards to 70 ± 10% for 2,3,7,8-TCDD, 90 ± 10% for OCDD, and 60 ± 10% for 2,3,7,8-TCDF. The samples were extracted and analyzed

in batches consisting of four or five samples, some of which were duplicates, and a method blank. Various standard solutions containing known amounts of both analyte and internal standard were analyzed at a frequency of one standard for every three samples. The final volume of sample extract was adjusted so that the amount of analyte was within the calibration range. The extent of dilution that was required was determined on the basis of preliminary analyses. In this way, the large range of concentration was handled without contaminating the instrumentation and cross contaminating the samples. For all samples, the measured isotopic ratios of the molecular ion clusters were consistent with their theoretical values. Results of procedural blanks and duplicate analyses are presented in Table I. DDD analyses were carried out as previously described (14), modified to include capillary column GC with peak assignments confirmed by alkali treatment of selected extracts to produce dehydrochlorination products (20). Radionuclide analyses were carried out by $\gamma$ spectrometry using lithium-drifted germanium and intrinsic germanium detectors with multichannel analyzers. All concentrations of chlorinated hydrocarbons and activities of radionuclides are reported on a per dry weight of sediment basis.

*Results and Discussion*

**Sample Collection and Dating.** In 1985 and 1986, we collected sediment core and suspended particle samples from the Passaic River and adjacent estuaries. Sediment core sections were analyzed for the $\gamma$-emitting radionuclides $^{7}Be$ and $^{37}Cs$ to establish the particle deposition histories at our various coring sites. As a result of the short

**Table I. Chlorinated Dibenzodioxin and Dibenzofuran Data[a]**

| sediment core[b] | depth, cm | 2,3,7,8-TCDD, ppt | OCDD, ppb | 2,3,7,8-TCDF, ppt |
|---|---|---|---|---|
| A1 | 0-2[c] | 20 | 8.0 | 24 |
| | 28-32[d] | ND (60) | 22 | 200 |
| B1 | 0-2[c] | 130 | 11 | 130 |
| C1 | 0-2[c] | 300 | 12 | 160 |
| D1 | 0-2[c] | 730 | 9.4 | 440 |
| | 2-4 | 1800 | 23 | 470 |
| | 24-28 | 660 | 19 | 390 |
| | 48-51[d] | 7600 | 24 | 3100 |
| D2 | 108-111 | 21000 | 38 | 4500 |
| E1 | 0-2[c] | 310 | 3.1 | 290 |
| F1 | 0-2 | 180 | 4.8 | 220 |
| | 4-6 | 1200 | 10 | 580 |
| | 12-16 | 680 | 7.5 | 370 |
| | 24-28[d] | 1100 | 11 | 300 |
| | 28-32 | 1100 | 5.5 | 530 |
| | 32-36 | 390 | 5.6 | 190 |
| | 32-36[e] | 390 | 5.7 | 190 |
| F2 | 32-36 | 2900 | 42 | 730 |
| | 40-44 | 93 | 5.5 | 140 |
| | 48-52 | ND (41) | 4.4 | 80 |
| F3 | 0-2[c] | 230 | 4.7 | 180 |
| H1 | 0-2[c] | ND (36) | 5.5 | 150 |
| H2 | 20-24[d] | 150 | 5.9 | 300 |
| I1 | 2-4[c] | 75 | 5.3 | 150 |
| J1 | 4-8 | 190 | 31 | 1200 |
| | 28-32 | ND (22) | NA | ND (32) |
| K1 | 2-4 | 2700 | 13 | 1400 |
| | 2-4[e] | 2500 | 15 | 1400 |
| L1 | 0-2 | 430 | 14 | 490 |
| Suspended Matter Samples | | | | |
| site G[c] | | 260 | 9.0 | 380 |
| site J[c] | | 120 | 13 | 220 |
| Blanks[f] | | | | |
| method blank 1 | | ND (42) | 0.18 | ND (17) |
| method blank 2 | | ND (61) | 0.61 | ND (53) |
| filter blank | | ND (17) | ND (1.8) | ND (35) |

[a] ND indicates none detected and is followed in parentheses by the detection limit. NA indicates not analyzed. [b] All samples in this table and in other publications from the Lamont laboratory can be unambiguously identified by control numbers available from the authors. [c] These samples are from the 1985 ± 1 year time horizon defined in the text. [d] These samples are from the mid-1960s time horizon defined in the text. [e] These results are from duplicate extraction and analysis of separate sample aliquots. [f] Blank concentrations are based on 1 g, the approximate sample size. Method blanks are results obtained with no sample. Filter blank results are from analysis of an unused quartz fiber filter similar to those used to collect the suspended matter samples.

half-life of [7]Be (53 days), detectable activity of this cosmic ray produced radionuclide is characteristic of both suspended matter samples and near-surface sediment samples containing a significant component of particles deposited within approximately 1 year prior to sample collection. [137]Cs, derived as fallout from atmospheric testing of large nuclear weapons, first entered natural water systems on a global scale in significant amounts in approximately 1954. Its presence in a sediment sample usually indicates an appreciable component of post-1954 deposition. In cores with continuous and relatively rapid sediment accumulation, the maximum levels of fallout ^{137}Cs can be associated with the years of peak fallout delivery (1963-1964) (12, 21-23).

On the basis of our radionuclide results, sets of samples were chosen at two different time horizons throughout the study area. All of the sediment core samples were dominated by fine-grained particles and had similar levels of [40]K, a natural radionuclide enriched in clay minerals relative to quartz sands. This indicates that the differences in contaminant levels among our samples were not significantly influenced by differences in sediment characteristics. Samples from within ~1 year of 1985 were either suspended matter or [7]Be-bearing sediment core sections. Sediment cores from four sites provided samples from a mid-1960s time horizon defined by maximum levels of fallout [137]Cs (Figure 1). An additional constraint on our chronologies in the Passaic River–Newark Bay system is provided by a minor, but consistent, near-surface ^{137}Cs maximum (Figure 2) that we associate with the highest recorded freshwater discharge of the Passaic of the past 50 years, which occurred in April 1984 (24). The 5-day discharge for 6 April through 10 April, 1984, was 40% higher than the next largest recorded discharge for any 5-day period between 1940 and 1988. We hypothesize that the record flow would have been accompanied by unusually high suspended matter concentrations that would inhibit desorption of ^{137}Cs from particles carried into the river from the drainage basin.

**Time Horizon Data.** Results of PCDD analyses (Figure 1) indicate that the 80 Lister Ave. plant was a major source of 2,3,7,8-TCDD to the natural water systems of the study area. At each time horizon, the highest concentrations of 2,3,7,8-TCDD were found on particles from sampling site D, adjacent to the plant. At this site and also in Newark Bay at site F, the mid-1960s samples were several times more contaminated with 2,3,7,8-TCDD than their respective mid-1980s samples. We attribute this pattern in space and time to the production of 2,4,5-T at the 80 Lister Ave. plant from about 1948 to 1969. Sampling site A is isolated from this particular industrial source by the Dundee Dam and had levels of 2,3,7,8-TCDD ~2 orders of magnitude lower than site D. While the mid-1980s' data (Figure 1) suggest the possibility of an additional source of 2,3,7,8-TCDD to the Hackensack River, some of the contamination at sampling sites B and C could also have been derived from the 80 Lister Ave. plant. During our sampling, salinities measured at the upper Hackensack station (site B) were up to a third of those observed in Newark Bay, indicating significant tidally driven upstream transport in the Hackensack River estuary. Also noteworthy were the relatively low levels of 2,3,7,8-TCDD found in New York Harbor sediments at site H. The substantial inputs of industrial contaminants to the harbor, evidenced by the high levels of PCBs and trace metals found in these same samples (25), do not alter the general trend of 2,3,7,8-TCDD levels decreasing with distance from Passaic River site D.

**OCDD and 2,3,7,8-TCDF.** In each of our samples, the level of OCDD was many times higher than that of 2,3,7,8-TCDD (Table I, Figure 1). While OCDD was the most abundant PCDD congener reported in the 80 Lister Ave. soil sample (5), the rather poor correlation between OCDD and 2,3,7,8-TCDD levels in our samples ($R^2 = 0.36$, Figure 3) indicates that there is a significant regional source for OCDD, a source that is depleted in 2,3,7,8-TCDD relative to the local industrial source. Combustion and the use of pentachlorophenol, a common wood preservative, are the most likely candidates for this regional PCDD source (10).

A much higher correlation was found between the levels of 2,3,7,8-TCDF and 2,3,7,8-TCDD in our samples ($R^2 = 0.87$, Figure 3). This suggests that the 80 Lister Ave. site was a major source of 2,3,7,8-TCDF to the natural waters of our study area. Similar to 2,3,7,8-TCDD, 2,3,7,8-TCDF can be produced as a contaminant during sodium 2,4,5-
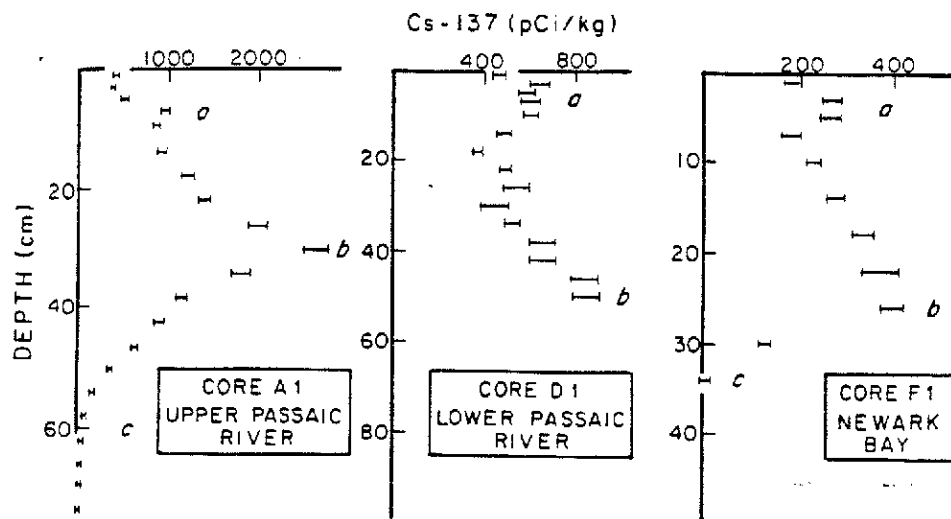
Cs-137 (pCi/kg)

Figure 2. $^{137}$Cs profiles in sediment cores from sites A, D, and F. Horizon *a* is the near-surface maximum (1984); *b*, we associate with the fallout maximum (1963–1964); *c* corresponds to the initial input of significant fallout (about 1954). Horizontal error bars indicate one standard deviation based on γ-counting statistics. A fourth core (H2) that provided a mid-1960s sample has been described elsewhere (25).
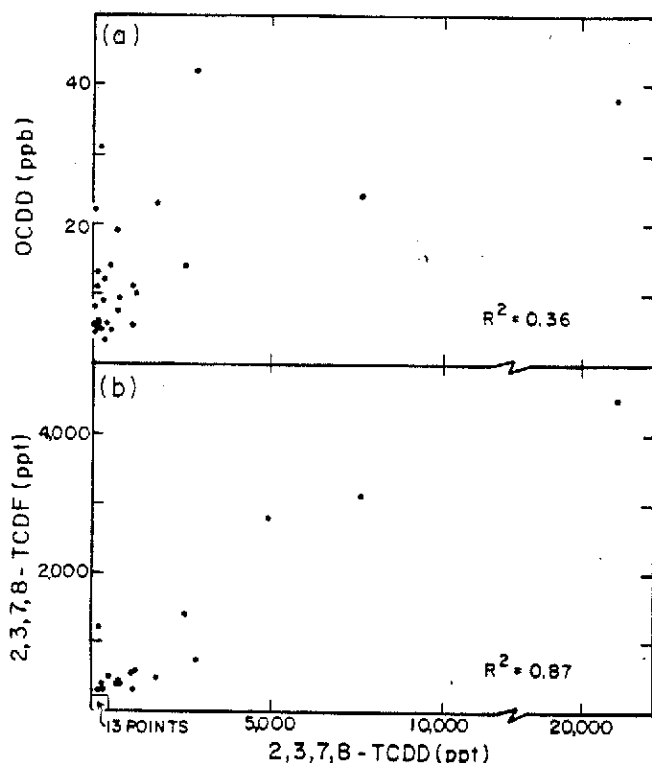


Figure 3. Plots of (a) OCDD and (b) 2,3,7,8-TCDF concentrations versus 2,3,7,8-TCDD concentrations for all the samples listed in Table 1. Correlation coefficients ($R^2$) were derived from linear least-squares analysis.



Figure 4. Chronologies of *p,p'*-DDD and 2,3,7,8-TCDD concentrations in Newark Bay sediments from sampling site F, cores F1 and F2. Approximate dates were assigned on the basis of the $^{137}$Cs profiles, utilizing the time horizons described in the text. Periods of production of DDT and 2,4,5-T at the 80 Lister Ave. plant are indicated by the arrows.

trichlorophenate synthesis (*1*) and was found at elevated levels in the 80 Lister Ave. soil sample (*5*).

**Chronological Data.** A more detailed chronology of 2,3,7,8-TCDD levels was developed for Newark Bay site F from two sediment cores. Core F1 penetrated to sediments deposited in approximately 1954 (Figure 2) while core F2 had a longer time record with deeper sections containing no detectable $^{137}$Cs, indicating pre-1954 deposition. Since DDT was also synthesized at 80 Lister Ave., the cores were analyzed for *p,p'*-DDD, which is produced in natural systems via reductive dechlorination of *p,p'*-DDT and is persistent in anoxic sediments (*14*). Results of these analyses (Figure 4) indicate that production of DDT at 80 Lister Ave. was the dominant historical source of DDT-related compounds to Newark Bay
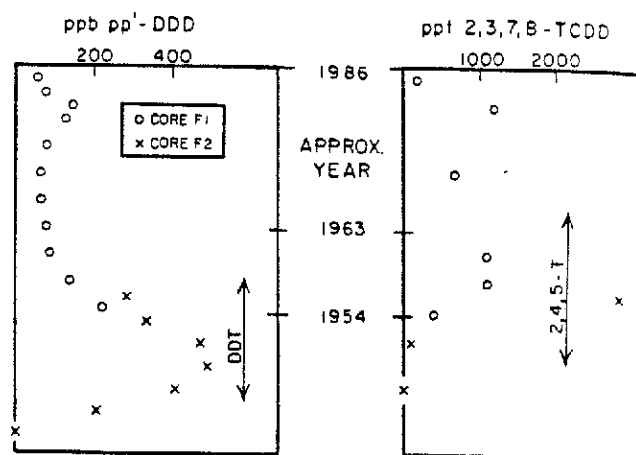
sediments over the past four decades.

Although *p,p'*-DDD is ubiquitous in sediments of natural water systems, the chronological detail of the Newark Bay profile is unique. DDT-related compounds in dated sediment cores from other natural water systems were generally first detected at low levels in the early 1950s and subsequently increased in concentration, reaching peak levels in the 1960s or 1970s (*12, 25*). In the Newark Bay cores, peak levels of *p,p'*-DDD are observed prior to 1954, consistent with production records for the 80 Lister Ave. plant. These records indicate synthesis of ~100 million lb of DDT, commencing prior to the end of World War II and terminating in 1958–1959 (*2, 3*). The near-surface maximum of the early 1980s coincides with the record Passaic River discharge in the spring of 1984 that flooded the plant and was the probable cause of the similar perturbation of $^{137}$Cs levels (Figure 2).

The 2,3,7,8-TCDD concentration profile derived from these cores, although somewhat lacking in detail, substantiates our linking of the sediment chronology and time horizon data with production records for the 80 Lister Ave. plant. Compared to *p,p'*-DDD, which traces site activity that commenced prior to the end of World War II, the profile shows a later onset of significant 2,3,7,8-TCDD

contamination consistent with production of 2,4,5-T beginning approximately in 1948. The maximum level of 2,3,7,8-TCDD contamination occurs during the period of active 2,4,5-T production and the sample showing the near-surface maximum in $^{137}$Cs and $p,p'$-DDD levels also contains significantly higher levels of 2,3,7,8-TCDD than the adjacent samples that have been analyzed.

Efforts to obtain a complete chronology for the lower Passaic River at site D, near the 80 Lister Ave. plant were not as successful. Core D1 provided the data for Figure 1, but did not penetrate into sediments deposited prior to the fallout maximum (Figure 2). Core D2 is noteworthy because its bottom section (108–111 cm) contained 21 000 ppt 2,3,7,8-TCDD, the highest concentration in any sample that we have measured (Table I). The $^{137}$Cs and 2,3,7,8-TCDD data are consistent with deposition of this sample during the mid to later stages of active 2,4,5-T production at 80 Lister Ave., from the late 1950s to early 1960s.

**Sediment Budget.** A measure of the significance of the 2,3,7,8-TCDD contamination is provided by some first-order sediment budget calculations. From our data on Newark Bay samples (Table I, sites E–G, K, and L), we estimate that the average fine-grained sediment deposited in the bay during the past 40 years contained between 600 and 1200 ppt 2,3,7,8-TCDD. On the basis of a sediment budget of Suszkowski (26), Olsen et al. (27) estimated the annual deposition of fine-grained sediments in Newark Bay at $1.7 \times 10^8$ kg/year. This yields a total deposition of 4–8 kg of 2,3,7,8-TCDD in Newark Bay over the past 40 years. This total places our study area among some of the most significant incidents of 2,3,7,8-TCDD contamination. For comparison, estimates of the amount of 2,3,7,8-TCDD released in the well-known cases of Seveso, Italy, and Times Beach, MO, are about 0.25 and 6 kg, respectively (1).

Most of the fine-grained sediment deposited in Newark Bay is subsequently removed via maintenance dredging of shipping channels (26, 27). Prior to 1970, when the most highly contaminated sediments were being deposited, the dredge spoils from this region were disposed of primarily in upland sites adjacent to the bay, "generally as fill material which was subsequently used for development" (26). Since 1970, most of the dredge spoils have been dumped in the Atlantic Ocean at a site located ~10 km off the New Jersey coast (26, 28). In preliminary analyses of sediments from the vicinity of that site, we have measured 2,3,7,8-TCDD levels of up to a few hundred ppt.

## Conclusions

Using a multitracer approach, we have described a major incident of 2,3,7,8-TCDD contamination in sediments of New Jersey estuaries. The dominant source of this compound appears to be a single chemical manufacturing facility. The high levels observed in sediments of the lower Passaic River and Newark Bay will have a major impact on the future management of these estuaries. The current practice of subaqueous disposal of sediments dredged from these waters at a coastal ocean dumpsite provides a significant and perhaps dominant transport of 2,3,7,8-TCDD to the continental shelf of the northeastern United States. This study also establishes the persistence of 2,3,7,8-TCDD and 2,3,7,8-TCDF in anaerobic sediments on a time scale of several decades.

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# Phenyltins in Water, Sediment, and Biota of Freshwater Marinas

## Karl Fent* and Judith Hunn

Swiss Federal Institute for Water Resources and Water Pollution Control (EAWAG), CH-6047 Kastanienbaum, Switzerland

■ A series of phenyltins and butyltins were determined in the water column, sediment, and biota of two freshwater marinas of Lake Lucerne, Switzerland. Considerable concentrations of triphenyltin (TPT), diphenyltin (DPT), and monophenyltin (MPT) were found for the first time in all the compartments. In addition, tributyltin (TBT), dibutyltin (DBT), and monobutyltin (MBT) occurred in significant concentrations. During 1988-1990, aqueous TBT concentrations followed a seasonal pattern with increases of up to 752 ng/L in late spring, followed by a successive decrease until winter, when concentrations remainded around 100 ng/L. TPT and TBT concentrations decreased during the observation period. Of the total aqueous TBT, 95-99% was present in the dissolved phase. In mussels *Dreissena*, TPT and TBT residues ranged up to 3.88 and 9.35 µg/g, respectively. Vertical sediment core profiles showed highest TPT and TBT concentrations of up to 107 and 2043 µg/kg, respectively, in the top with decreasing values with depth. Dating of the core and the occurrence of only low concentrations of DBT and MBT indicate that TBT is conserved in these sediments over a time period of years.

## Introduction

Organotin compounds are entering the marine and freshwater environment from their use in antifouling paints. Small amounts of these biocides are released continously from vessels into the water, thereby preventing attachment of organisms. Municipal and industrial wastewater, sewage sludge, and landfill leachates are additional organotin sources (1, 2). Thus far, attention has mainly been given to tributyltin (TBT), although triphenyltin (TPT) has also been employed as a cotoxicant with TBT in some long-performance antifouling paints. Contamination of aquatic systems by TPT and the aquatic toxicity of this compound are only little known. TPT and TBT are both highly toxic to aquatic life (3). TBT is particularly toxic to molluscs (oysters) and gastropods (3-8), leading to declines of dog whelk populations on various coasts (8). Chronic toxic effects on oysters (shell deformation) (9) and marine gastropods (sterilization of females) occur at aqueous concentrations of a few nanograms per liter (8), and most susceptible marine algae (10, 11) and zooplankton species (12-14) were negatively affected at a few hundred nanograms per liter.

In contrast to TBT, concentrations of TPT in the marine and freshwater environment are fairly unknown. In-

creased levels of TBT in water, sediment, and biota have been linked primarily to boating activities. In the water column, TBT residues were reported to lie in the high nanograms per liter range for seawater marinas, and in the low to medium nanograms per liter range for open water (9, 15-19). TBT residues in the sediments were found to be considerably higher, typically in the range of ~200-1000 µg/kg (15-17), with decreasing levels with depth (20). In water, degradation of TPT and TBT takes place. TPT was shown to be photodegraded to diphenyltin (DPT) (21), and TBT was biodegraded by successive dealkylation reactions leading to dibutyltin (DBT) as the principal degradation product with lesser amounts of monobutyltin (MBT) (22, 23). In sediments, TBT degradation was reported to be much slower with half-lives of 4-5.5 months (20, 22).

To date, little is known about the occurrence, temporal variation, and behavior of organotin compounds in freshwater systems (15-17), especially in respect to phenyltins. The purpose of this study was to determine the presence, partitioning, and fate of phenyltins and butyltins in different compartments of freshwater marinas and detect and monitor seasonal variations and trends throughout 1988-1990. The results document for the first time a series of phenyltin residues in water, sediment, and biota. Although the origin of TPT is attributed to antifouling paint leachates, this compound has a growing importance as an agricultural pesticide prone to contaminating the aquatic system by leaching and runoff. This suggests that the presented findings are applicable to more than this particular site. Our study also gives for the first time detailed phenyltin and butyltin sediment profiles in conjunction with $^{137}$Cs profiles. The sedimentary record suggests that TBT is conserved in these sediments over time periods of years.

## Experimental Section

**Study Sites and Sampling Procedure.** During 1988, 1989, and 1990, samples were taken in the 2.5-3 m deep marinas Lucerne (SEG) and Stansstad (STA) of the oligotrophic Lake Lucerne, located in the central part of Switzerland (Figure 1). The marinas were selected on the basis of different size and construction. Marina SEG was constructed in 1978, has berths for 456 vessels, and is well flushed. Marina STA has berths for 242 vessels, was constructed in 1965, and has a narrow entrance resulting in poor flushing. Water samples were always collected at the same location within the marinas adjacent to the vessels at midmonthly intervals. A stainless steel

* Present address during sabbatical leave: Woods Hole Oceano-

capacitances were 0.20 F M⁻² and all inner-layer capacitances were 1.40 F M⁻² (except for two whose values were 1.25 F M⁻²).

Additionally, Drs. Dzombak and Hayes criticize our paper because the interrelationship among electrolyte sorption constants, acidity constants, and site density is not discussed. They present TLM parameters for a *single* data set using FITEQL and a variety of *assumed* site densities, inner-layer capacitances, and acidity constants. Theirs and similar results (4) show very high correlations between electrolyte binding constants and site density, lesser but significant correlation between inner-layer capacitance and electrolyte binding constants, and no correlation between acidity constants and any other model parameters. Drs. Dzombak and Hayes recognize that the method used by Hayes et al. (4) to determine TLM parameters completely compensates for variation in site density by allowing the electrolyte binding constants to vary and that a relationship between site density and surface acidity constants will only hold if capacitance values and electrolyte binding constants are similar for the various TLM parameterizations. *This, is in fact, the case for the studies we evaluated.* In our evaluation of TLM studies (1), we found a strong correlation between site densities and acidity constants. Our conclusion regarding relationships between determinations of site density and acidity constants was a generalization that is consistent with the studies we evaluated. TLM parameterization using widely different density, acidity constant, capacitance, etc., were not found in the literature; therefore, the effects of a wide range of values of these TLM parameters could not be determined from available experimental studies.

In our development of sets of TLM constants for cation adsorption, we calculated values of $K^{SC}$ from the values of $K^{int}$ and $K_{a2}^{int}$ used by the original investigators. Values of $K^{SC}$ so derived were converted to a uniform set of $K^{int}$ values using a single value of $K_{a2}^{int}$. The values presented are consistent with outer- and inner-layer capacitances of 0.2 and 1.4 F M⁻², respectively, for iron oxides. Outer- and inner-layer capacitances of 0.2 and 2.4 F M⁻², respectively, were used for manganese oxides. We have previously provided (1) acidity constants and electrolyte binding constants.

We are pleased that Drs. Dzombak and Hayes echo our earlier recommendation, even though they apparently did not read our conclusion (2) that "The methods used to derive values of p*$K^{int}$ are often poorly defined, subjective, and differ among investigators. Much of the uncertainty associated with p*$K^{int}$ could be removed if all the experimental work reported in the literature were re-evaluated using a single set of objective criteria for deriving values of p*$K^{int}$".

The constants we presented (1) should not be viewed as the "final and correct" set of TLM parameters; however, our contribution represents, in our opinion, a significant improvement and is the most useful compilation of TLM parameters currently available in the literature. Furthermore, it is unlikely that a significantly better set of values will be available without the type of major recalculation effort we suggested in our earlier report (2). Additionally, though there is indeed a wide availability of very powerful microcomputers, the parameterization of the nonlinear TLM is not nearly as simple as the comments of Drs. Dzombak and Hayes would suggest, especially given the necessity of ensuring physically meaningful values of TLM parameters.

In summary, we contend that the values of $K^{int}$ presented are internally consistent with the limitations and uncertainties we have previously identified (1, 2).

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**Robert W. Smith**

Idaho National Engineering Laboratory
Idaho Falls, Idaho 83415


**Everett A. Jenne\***

Pacific Northwest Laboratory
Richland, Washington 99352

## Comment of "A Major Incident of Dioxin Contamination: Sediments of New Jersey Estuaries"

SIR: Set forth below are our comments on the paper by Bopp et al. (1) on dioxin contamination in the Newark Bay area. The authors were using a very limited data base to cover a broad area (over 30 river miles). We disagree that this dated core study, involving three cores, can conclude anything about a specific source. While it may be true that dioxin contamination in the 1950s' and 1960s' sediment is greater than recent sediment levels, there are inadequate data to conclude that "the dominant source of this compound appears to be a single chemical manufacturing facility". The limited data presented in this paper seem only to promote misconceptions and do not consider the actual validity and interpretive usefulness of the data.

Scientific studies should rely on a more significant number of data points, use only independently validated analytical results, fully report all data, consider other sources, consider localized sedimentation rates, and qualify or limit conclusions to the extent supported by the data. Science should be used to identify and report fact-based conclusions. Reporting only the partial data that are "consistent" with a hypothesis is scientifically misleading.

(1) The authors claimed the 80 Lister Ave. site was the dominant source of DDT and its derivatives. The authors do not explain their large-volume filtered sample data which showed DDD concentrations in the Arthur Kill of over 3-fold greater than any other location (590 vs 181 ppb) and DDT concentrations in the Arthur Kill of almost twice (260 vs 161 ppb) the concentration of any other location reported. These data were not consistent with the authors' 80 Lister Ave. source (2).

(2) The authors' Figure 1 did not present all surface and near-surface sediment PCDD/PCDF data. The 1985 figure should have included additional surface sediment and suspended matter results reported in Table I and not just selected data. When sample K (2700 ppt 2,3,7,8-TCDD 2–4 cm) is shown, the possibility of other 2,3,7,8-TCDD sources in the center to southern sections of Newark Bay

becomes apparent. This datum directly contradicts the authors' statement of "... the general trend of 2,3,7,8-TCDD levels decreasing with distance from the Passaic River site D" (80 Lister Ave.). When 2,3,7,8-TCDF concentrations are plotted on this same drawing, potentially significant sources are identified at locations K (1400 ppt) and J (1200 ppt) which greatly exceed the 440 ppt reported at 80 Lister Ave. (location D). The two reported suspended matter results show a TCDD/TCDF ratio of 0.68 and 0.55 vs approximately 2.0–4.0 in sediments at the alleged source location D. These data, if illustrated, would show that there is not a general trend from the 80 Lister Ave. site.

(3) The authors cannot draw conclusions from the age of sediments at location D1 because they did not confirm a $^{137}$Cs maximum or the start of the pre-$^{137}$Cs fallout sedimentation in this core, which is needed for dating. They report $^{137}$Cs data in their paper at 51 cm, which was assumed to be a maximum in core D1. Adjacent sample D2 in ref. 2 was reported by the authors to have a $^{137}$Cs value of 1055 pCi/kg at 92–96 cm vs 821 pCi/kg at 48–52 cm, which was claimed to be the maximum $^{137}$Cs value representing the 1963 time period. Therefore, the depth of 92–96 cm was closer to the maximum $^{137}$Cs than the 48–52 cm claimed by the authors.

(4) The authors presented several unsupported or poorly supported descriptions of other data to discuss sediment transport hypotheses. These statements should have been further qualified as noted:

(I) The authors' suggestion that river flooding at the 80 Lister Ave. site in 1984 was the cause of increased DDT levels is without support. The 80 Lister Ave. soils were controlled by surface covers by the summer of 1983 (3) under the supervision of the New Jersey DEP. There is no documentation that runoff of DDD/DDT from the site caused the suggested increase in Newark Bay sediment concentrations. As stated previously, there is little evidence that the authors considered other sources of DDT/DDD in their analyses.

(II) The authors suggest that the manufacturing building fire in 1960 at the 80 Lister Ave. site caused the high OCDD, OCDF, and TCDF concentrations found in the single site soil sample in their analyses used to characterize the site. The single surface soil sample was collected from an area where the 1960 manufacturing building was demolished, filled, and regraded as part of the plant reconstruction. Therefore, the soil area tested was most likely fill material placed after 1961. There is no basis, just supposition, that the fire caused the elevated OCDD/OCDF/TCDF concentrations detected in the soil sample. Also, there was no pathway to the river documented for the soil sample.

(III) The authors' statement that the 2,3,7,8-TCDD concentration profiles are "somewhat lacking in detail" is a considerable understatement. Due to the limited dating at core location D1, no significant dated sediment dioxin data are presented to compare between locations. The fact is that an attempt was made to compare two cores below the Dundee Dam over an area covering almost 30 river miles to demonstrate a source link. This attempt was completely inadequate and inappropriate.

(IV) The authors also claim 2,4,5-T production began in 1948. 2,4,5-T processing did not begin at the plant until March 1951, per ref 3.

(V) The authors did not discuss the sampling period differences between the August 1985 to October 1986 samples (2). They should have explained the possible impact that the timing of the sampling and analysis activities had on the validity of the results.

(5) The authors' data may have demonstrated relative dating of 2,3,7,8-TCDD contamination, but there was no exclusive source determination. Prior to the discovery of dioxins in Newark Bay, many sources had been curtailed. Many 2,4,5-T registered uses ended in 1970. Esposito et al. (ref 4, p 98), for example, identified 2,4,5-T as being registered for application to lakes, ponds, and ditch banks until 1970. This end of registration date coincides with the timing of the 1969 closure of the 80 Lister Ave. site. The limited data set presented in this article contained insufficient data to demonstrate a consistent trend of 2,3,7,8-TCDD, TCDF, or DDT concentrations decreasing or increasing as a function of distance from the 80 Lister Ave. site. In fact, the TCDF and DDT data presented (in the authors' Table I) are instead suggestive of other origin areas.

Other potentially significant 2,3,7,8-TCDD sources identified in refs 4 and 5 were available to the authors. There was no mention or evaluation in the paper of the contributions from these other sources. The authors have also not considered the many waste handling firms, even those found to have had direct discharges to the Newark Bay system (Chemical Control on the Elizabeth River, for an example). New Jersey claimed to be the first or second largest chemical producer in the country during the 1950s–1960s. The idea of identifying a single dominant source of 2,3,7,8-TCDD for the entire watershed with only two core analyses and without an adequate site characterization is without support.

Some of the major potential sources of dioxins in the Passaic River have not been investigated (6). One known site not considered by the authors is Prentiss Drug. The New Jersey Department of Environmental Protection (NJDEP) (4) reported that Prentiss Drug has over 200 ppb 2,3,7,8-TCDD present. The authors need more than two core samples to confirm a single source when such significant other potential sources are present. There are many Newark facilities and other Passaic River watershed, and Newark Bay watershed, facilities that have not been investigated as major manufacturing sources of dioxin.

(6) The authors did not consider localized dredging and sedimentation rates around their suspected source. A review on Army Corps of Engineers records indicates the site area (location D) was last dredged in 1937, as was reported in the authors' ref 3. Army Corps of Engineers' sounding data and a 1986 report to the NJDEP (6) show that since the 1940s over 20 ft of sediment has accumulated adjacent to the site. This same area appears to be the largest sedimentation trap on the Passaic River during the 1940–1970 time frame. The sediment trap has contained locally generated particulates, as well as having acted as a sedimentation area for particulates generated in other sections of the river.

The authors' data confirm that the area adjacent to the 80 Lister Ave. site is highly successful in collecting organic contamination with the sediments. The 8580 ppb Aroclor 1254 and 21000 ppb Aroclor 1242 in Passaic River core D2 (2) is 3–5 times higher than any other Passaic, Hackensack, Newark Bay, or Kill Van Kull data points reported by the authors (2). No Aroclors are associated with the authors' suspected source site (3) however.

These comments address only some of the obvious technical deficiencies in the Bopp et al. paper. This paper used bad scientific practices in preselecting a hypothesis and then presenting, or highlighting, only those data which were consistent with the hypothesis. Most disconcerting is the possibility that this type of presentation could cause other researchers to misdirect their studies and delay the

day when this watershed is truly understood.

**Registry No.** DDT, 50-29-3; 2,3,7,8-TCDD, 1746-01-6; 2,3,7,8-TCDF, 51207-31-9; 2,4,5-T, 93-76-5.

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**Hadley Bedbury**

Chemical Land Holdings, Inc.
717 North Harwood Street
Dallas, Texas 75201

SIR: Our general response to the comments of Hadley Bedbury is to urge interested parties to carefully read the paper. We respond to specific comments as follows:

1. Our paper discusses the sources of DDT-derived compounds to sediments of Newark Bay (not the Arthur Kill). The dominant feature of our $p,p'$-DDD chronology from Newark Bay (Figure 4) is the pre-1954 maximum of 490 ppb. The timing of this maximum distinguishes Newark Bay from other natural water systems for which DDT-derived compound chronologies have been reported (1–3) and is consistent with an 80 Lister Ave. source.

In contrast to the mid-1980s' Arthur Kill sample that contained 590 ppb $p,p'$-DDD, our four Newark Bay suspended particle samples contained 103, 107, 110, and 112 ppb (4). The Arthur Kill sample provides evidence of a very recent source of DDT-derived compounds to waters around Staten Island. We plan to utilize this tracer to place limits on the amount of up-estuary (into Newark Bay) transport of particle-associated contaminants that occurs in the system.

2. This comment indicates that an essential point has been missed. Not all near-surface sediment samples qualify as having been deposited within a year or two of core collection. As mentioned in our response to the other letter, net particle accumulation rates in estuaries can vary over short distances from zero to over 10 cm per year. This is precisely why, for each core, an independent indicator of the time of deposition (such as Be-7 activity or a Cs-137 activity profile with depth) is needed. In the case of core K1, Cs-137 activity was maximum in the 0–2-cm sample and penetrated to a depth of only 6 cm (4). This could indicate either very low net accumulation or perhaps loss of the core top at this site. In either case, the 2–4-cm section from this core would be expected to contain a significant component of particles and associated contaminants deposited between the early 1950s and the mid-1960s. This would account for the high level of 2,3,7,8-

TCDD in this sample compared to our mid-1980s' samples and also explain the high 2,3,7,8-TCDF level.

3. This argument depends on the assumption of similar net particle accumulation rates for cores D1 and D2. A closer inspection of the data (4) would have revealed evidence that D2 has a significantly faster accumulation rate. The 0–4-cm sample in this core had a Be-7 activity of 2126 ± 192 pCi/kg. The 0–2-cm sample of core D1 had a significantly lower activity (716 ± 236 pCi/kg) and Be-7 was not detected in the 2–4-cm sample (124 ± 239 pCi/kg). Our assignment of a mid-1960s' date to the 48–51-cm (bottom) section of core D1 is consistent with the Be-7 data and with the location of the "a" horizon and the Cs-137 profile shown in Figure 2.

4. I. The signal that we associated with the 1984 flood event, including the elevated level of $p,p'$-DDD in core F1, is primarily a dating tool that was used to define our "a" horizon. It is clear from our Figure 4 that the perturbation in levels of DDT-derived compounds that we associate with this event is minor compared to the pre-1954 maximum levels. In discussing possible sources of the increased levels of $p,p'$-DDD, we felt that it was appropriate to note the flooding of a facility where approximately 100 million pounds of DDT had been produced.

II. The soil sample analysis (5) was the only detailed PCDD characterization of the site that we found in the open scientific literature. It was necessary to indicate that both the fire and the manufacture of several additional chlorinated phenol products at the facility were probable contributors to the complex mixture of PCDDs in that sample.

III. Chronological data on 2,3,7,8-TCDD levels from cores F1 and F2 complement the $p,p'$-DDD chronology (Figure 4) and our time horizon data (Figure 1). Our interpretations rely on multiple tracers and the several lines of evidence presented in the paper.

IV. Initiation of 2,4,5-T production at the plant in 1951 instead of 1948 would not change our interpretation of the 2,3,7,8-TCDD chronology from Newark Bay cores F1 and F2 (Figure 4). If anything, the data are better explained by the later start of production.

V. "Sampling period differences" would be expected to have the greatest effect on our suspended particle samples. Based on contaminant analyses (4), such differences appear to be relatively minor. For example, our four Newark Bay suspended particle samples were collected in April 1985, August 1985, March 1986, and October 1986. Levels of $p,p'$-DDD ranged only from 103 to 112 ppb. Levels of $\gamma$-chlordane ranged between 23 and 35 ppb. Of the contaminants that were measured, only $p,p'$-DDT levels spanned as much as a factor of 2 (from 12 to 25 ppb).

5. These comments do not acknowledge the significance of our upper Passaic (site A) and New York Harbor (site H) time horizon samples. The low levels of 2,3,7,8-TCDD at these sites relative to our lower Passaic and Newark Bay sites require, as a minimum explanation, a significant point source of 2,3,7,8-TCDD to the lower Passaic. While interpretation of our data does not require another major source of 2,3,7,8-TCDD, we also did not rule out that possibility. Specifically, we stated that "the mid-1980s' data (Figure 1) suggest the possibility of an additional source of 2,3,7,8-TCDD to the Hackensack River".

6. The success of our approach depends on our ability to locate areas of rapid net sediment accumulation. Such areas will accumulate particle-reactive contaminants transported within the natural water system. For the case of PCBs cited in the comment, it is interesting to note that the sample with the second highest levels of Aroclor 1242

and 1254 components (*4*) was from site A on the Passaic, above the Dundee Dam. This suggests that downstream transport is a significant contributor to the PCBs accumulating in the lower Passaic. The similar analysis of 2,3,7,8-TCDD levels presented in our paper indicated that transport over the Dundee Dam was not a significant source of 2,3,7,8-TCDD to the lower Passaic. We maintain that contaminant analysis of dated core sections is one of the best tools available for studying the sources and fate of particle-associated contaminants in natural water systems.

**Registry No.** DDT, 50-29-3; 2,3,7,8-TCDD, 1746-01-6; 2,3,7,8-TCDF, 51207-31-9; 2,4,5-T, 93-76-5.

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**Richard F. Bopp**

Department of Earth and Environmental Sciences
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

SIR: Recently, Bopp et al. (*1*) reported on the levels and geographical extent of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (2,3,7,8-TCDD, dioxin) and related compounds in sediments collected from the Newark Bay estuary. The authors described a depositional profile in four sediment cores from the lower Passaic River and Newark Bay through measurements of *p,p'*-DDD and the radionuclides $^7$Be and $^{137}$Cs. They concluded that a former chemical manufacturing facility was the dominant source of 2,3,7,8-TCDD and a major source of 2,3,7,8-tetrachlorodibenzofuran (2,3,7,8-TCDF). Like Bopp et al., we have been interested in dioxin contamination of the Newark Bay estuary (*2, 3, 12*). Accordingly, we feel it would be useful to discuss a few points raised by Bopp et al. (*1*).

First, the results of their linear least-squares analyses shown in Figure 3 for 2,3,7,8-TCDD, 2,3,7,8-TCDF, and OCDD concentrations in sediments are not consistent with the authors' hypothesis that chemical profiles in Newark Bay sediment cores could be correlated with industrial activity during discreet periods of time (*1*). The data used in their calculations were derived from 29 dioxin measurements taken, in most cases, at different depths ranging from 0–2 cm to as deep as 108–111 cm in 11 sediment cores. Statistical correlations among 2,3,7,8-TCDD, 2,3,7,8-TCDF, and OCDD concentrations should have been calculated using data from the same depths; i.e., the same relative time horizons asserted by the authors based on their radionuclide measurements. Using the nine samples from Table I (*1*) that were claimed by the authors to be associated with the 1985 ± 1 year time horizon (0–2-cm

depth), we calculated a less significant correlation between the concentrations of 2,3,7,8-TCDD and 2,3,7,8-TCDF ($R^2$ = 0.69) than reported by the authors ($R^2$ = 0.87).

Second, the authors (*1*) asserted that dioxin analyses in sediment core sections showed that a single site was the dominant source of 2,3,7,8-TCDD to Newark Bay; however, this was not supported by their data. For example, of the 11 sediment core sampling stations shown on the map of the study area (Figure 1), only one site (site D) was located within 2 mi of the suspected source. Geochronologies using $^{137}$Cs appear to have been derived in only three sediment cores. The 2,3,7,8-TCDD and DDT profiles in Figure 4 (*1*) were derived from two cores at one sediment sampling station located nearly 5 mi from the former chemical manufacturing facility.

It is our opinion that these sampling stations were located too far apart to be able to relate chemical releases from any possible industrial source, including the former chemical manufacturing plant. Because many of the chemical, textile, and petroleum production and manufacturing activities along the waterway over the past 40 years (*4*) are known or suspected to be linked to the formation of dioxins (*5*), numerous potential sources of 2,3,7,8-TCDD were likely present within the heavily industrialized and populated Newark, NJ–New York City, NY, metropolitan area (*6, 7*). For example, the New Jersey Phase II Dioxin Investigation, completed in 1986, identified at least six industrial sites within the Newark Bay watershed with 2,3,7,8-TCDD soil concentrations greater than 1 part per billion (ppb) (*6*). At sites identified by the New Jersey Department of Environmental Protection and Energy (NJDEPE) or by the U.S. Environmental Protection Agency (USEPA) as part of the National Dioxin Study (*5*), elevated dioxin concentrations were measured in sediments from adjacent rivers, including the Hackensack River (*5–7*), Third River (*6, 7*), Elizabeth River (*5–8*), and Raritan River (*5–7*). Recently, we have shown that the 2,3,7,8-substituted dioxin patterns in numerous potential industrial and municipal outfalls, which are known to be present in the estuary, correlate with the isomer patterns observed in surficial sediment samples collected throughout Newark Bay (*2*).

Third, the authors gave the impression that the average concentration of 2,3,7,8-TCDD in soil at the former chemical manufacturing facility was 2000 ppb (*1*). The authors' information was obtained from a soil bioavailability study that described 2,3,7,8-TCDD concentrations in two soil samples from the Newark site (*9*). It was unclear from that study whether the samples were collected from the former chemical manufacturing site or from a neighboring scrap metal yard (*9*). The exact locations of those soil samples were not established in that study. Furthermore, virtually all sampling to date has focused on suspected hot spots, which represent less than 2% of the surface area of the site (*10, 11*). Our on-going work suggests that the amount of dioxin-contaminated soil that could have entered the lower Passaic River through runoff from the former chemical manufacturing facility is inadequate to account for the pervasive contamination described by Bopp et al. (*1*).

On the basis of the results of recent fingerprinting research, we have shown that dioxin contamination at various locations throughout Newark Bay is almost certainly due to contamination from many sources (*2, 3*). For example, we have demonstrated that the presence of one dioxin isomer, 1,2,8,9-TCDD, that was measured in bottom sediments and aquatic biota from Newark Bay is clearly due to the presence of numerous commercial, residential, municipal, and industrial sources (*3*). Furthermore, ad-

ditional studies conducted by our group have shown that the concentrations and distributions of dioxin in Newark Bay sediments are not unlike those found in sediments from other waterways located in heavily industrialized or populated areas (12).

The work conducted by Bopp and colleagues is representative of that which is needed to better understand the degree of contamination present in many of America's waterways. A number of studies will be needed to fully understand the distribution of chemicals in bottom sediments in the Newark Bay estuary and other areas. Their work illustrates the complexities of the sampling and analytical programs required, as well as the difficulties associated with the interpretation of the results. Hopefully, research of this type will encourage others to conduct comprehensive field investigations to characterize chemically-contaminated sediments in lakes, rivers, and streams.

**Registry No.** 2,3,7,8-TCDD, 1746-01-6; 2,3,7,8-TCDF, 51207-31-9; octachlorodibenzo-p-dioxin, 3268-87-9.

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**Richard J. Wenning***

ChemRisk—A Division of McLaren/Hart
1685 Congress Street
Portland, Maine 04102

**Dennis J. Paustenbach**

ChemRisk—A Division of McLaren/Hart
1135 Atlantic Avenue
Alameda, California 01984

SIR: We do not agree with the assertions of Wenning and Paustenbach concerning the correlation between the levels of 2,3,7,8-TCDD and 2,3,7,8-TCDF in our sediment core samples (our Figure 3). The highest levels of both compounds were found in samples that represent the period of appropriate industrial activity at the 80 Lister Ave. site, and we would expect some correlation to be maintained in more recent samples. In the Hudson River and estuary, for example, we have noted that the levels of particle-associated substances on sediments accumulating in depositional areas decreases with a half-time of a few years following curtailment of a direct input to the river (1). We interpret this response as a reflection of sediment transport, mixing, resuspension and burial within the river system. For a large input, a correlation between levels of two introduced contaminants could persist long after cessation of direct inputs. Additional inputs from the site that postdate the period of industrial activity would also contribute to preserving a correlation between contaminant levels in recently deposited sediment samples. We specifically discussed the record high flow in the Passaic River in the spring of 1984, which flooded the 80 Lister Ave. site, as a possible source of such inputs.

The observation of a somewhat less significant correlation between 2,3,7,8-TCDD and 2,3,7,8-TCDF levels for the mid-1980s' samples compared to the entire data set was to be expected. Exclusion of samples deposited in the 1950s and 1960s eliminates the highest levels of both 2,3,7,8-TCDD and 2,3,7,8-TCDF, enhancing the relative importance of other sources of TCDFs not related to TCDDs (e.g., PCBs).

It also appears that the authors have misinterpreted our dating information. The same depths in sediment cores do not necessarily represent the same time horizons. For example, radionuclide profiles have allowed us to identify the mid-1960s' time horizon as occurring at about 30 cm in core A1 and at about 50 cm in core D1. In estuaries, net sediment accumulation rates can vary from zero to more than 10 cm per year over short distances (2).

Concerning the sources of 2,3,7,8-TCDD to Newark Bay, we stated that "The dominant source of this compound appears to be a single chemical manufacturing facility". We take issue with the assertion that the conclusion is not supported by the data. The high levels of 2,3,7,8-TCDD found in the vicinity of the plant as well as the particularly high levels found at sites D and F for the mid-1960s' time horizon are certainly observations that support the hypothesis. Furthermore, the very high levels in the section of core D2 representing the late 1950s to the early 1960s are in accord with the hypothesis. We also disagree with the implication that 5 mi down-estuary is too long a distance for tracing an input of particle-associated contaminants. Again citing our past work on the Hudson River as an example, major deposition of particle-associated radionuclides released from the Indian Point power generating nuclear reactors occurs 40 mi down-estuary in New York Harbor (3).

Finally, with respect to dioxin "fingerprinting", we suggest that the authors analyze their own Newark Bay data (presented in their ref 2) in terms of the fraction of TCDDs represented by the single isomer 2,3,7,8-TCDD. In their most highly contaminated samples, the 2,3,7,8-isomer comprises most of the TCDDs. Our observations (4) suggest that dominance of the 2,3,7,8-isomer could be useful for distinguishing the TCDD contamination in Newark Bay sediments from that found in sediments of other waterways. In their calculation of toxicity equivalents, Wenning and Paustenbach (their ref 2) provide the rationale for focusing on this single isomer when considering PCDD contamination in Newark Bay. 2,3,7,8-TCDD dominates the dioxin-associated toxicity of their most

contaminated Newark Bay sediment samples.

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**Richard F. Bopp**

Department of Earth and Environmental Sciences
Rensselaer Polytechnic Institute
Troy, New York 12180-3590

## Comment on "Formic and Acetic Acids in Coastal North Carolina Rainwater"

SIR: The article by Avery et al. (*1*) presents interesting data on the concentrations of formic and acetic acids in precipitation samples. The paper contains calculations showing the contributions of the two acids to the acidity of the samples. These calculations are erroneous, and the first sentence in the abstract is not supported by the data.

As pointed out by Stumm and Morgan (*2*), parameters such as acidity must be defined at a reference level. Acidity measures the concentration of all species containing protons in excess minus the concentration of all species containing protons in deficiency of the proton reference level. The quantities mineral acidity and total acidity may be developed by applying this definition to different reference levels. For a solution containing a mixture of polyprotic acids, the generalized expressions for these quantities are given in eqs 1 and 2, where [H-Acy]

$$[\text{H-Acy}] = [\text{H}^+] - \sum_{i=1}^{n}\sum_{x=0}^{z-1}(z-x)[\text{H}_x\text{A}_i^{y-x}] - [\text{OH}^-] \quad (1)$$

$$[\text{HA}_t\text{-Acy}] = [\text{H}^+] + \sum_{i=1}^{n}\sum_{x=1}^{z}x[\text{H}_x\text{A}_i^{y+x}] - [\text{OH}^-] \quad (2)$$

is the mineral (or strong acid) acidity, [HA$_t$-Acy] is the total acidity, [H$^+$] is the hydrogen ion concentration, [H$_x$A$_i^{y-x}$] is the concentration of weak base $i$ coordinated with $x$ protons with charge $y - x$, [OH$^-$] is the hydroxide ion concentration, [H$_x$A$_i^{y+x}$] is weak base $i$ coordinated with $x$ protons and charge $y + x$, $n$ is the number of weak acids

in solution, $z$ is the number of protons that weak acid $i$ will release in a strong base titration, $y$ is the charge of the fully deprotonated species and $x$ is the number of titratable protons coordinated with the ion. Of course, acidity can also be defined at any intermediate reference level.

The authors did not state what type of acidity they were referring to in their paper. It appears the second of two unnumbered equations on page 1877 was used for the calculation of the contribution of formate to acidity

$$\% \text{ contribution of formate} = [\text{formate}]/[\text{H}^+] \times 100 \quad (3)$$

and a similar equation was used to calculate the acetate contribution. These calculations require the assumption that mineral acidity is equal to [H$^+$]. Due to the presence of weak acids in the samples, this assumption is probably not valid. Furthermore, eq 1 shows that formate and acetate anions *decrease* the level of strong acid acidity.

Calculations of strong acid and total acidity for the data found in Table II of Avery et al. (*1*) are presented here in Table I. The precipitation samples were assumed to be in equilibrium with atmospheric CO$_2$, yielding a constant concentration of 10 $\mu$equiv/L for carbonic acid. The p$K$ values of 3.75, 4.76, and 6.35 were used for formic, acetic, and carbonic acids. The contributions of carbonate as well as the effects of activity coefficients were ignored. Applying eqs 1 and 2 to the Avery et al. samples results in eqs 4 and 5. The three columns under the "acidity"

$$[\text{H-Acy}] = [\text{H}^+] - [\text{CHOO}^-] - [\text{CH}_3\text{COO}^-] - [\text{HCO}_3^-] - 2[\text{CO}_3^{2-}] - [\text{OH}^-] \quad (4)$$

$$[\text{HA}_t\text{-Acy}] = [\text{H}^+] + [\text{CHOOH}] + [\text{CH}_3\text{COOH}] + 2[\text{H}_2\text{CO}_3] + [\text{HCO}_3^-] - [\text{OH}^-] \quad (5)$$

heading indicate acidity calculated by first assuming it to be equal to [H$^+$], using eq 4, and eq 5. The final two columns show the contribution of formic and acetic acids to total acidity.

The calculations show first that the assumption that acidity is equal to [H$^+$] is poor for the solutions that were studied. [H$^+$] overestimates mineral acidity and underestimates total acidity. Second, the contributions of formic and acetic acids are significantly less than the 23% suggested by Avery et al. The highest contributions were for the G1 season (2.5 and 5.2%) while the overall average contributions were 2.0 and 4.2%. These calculations are based upon the simplifying assumptions noted above, and it is likely that there were other components to acid–base chemistry of the precipitation samples. The impact of other components on the mineral and total acidity cannot be predicted.

The statement that "ammonium ... is fully protonated and hence does not contribute to the hydrogen ion concentration" is also in error. If the species enters the

**Table I. Calculation of Acidity Functions and Contributions of Formic and Acetic Acids**[a]

| season | pH | formic acid | | | acetic acid | | | carbonic acid | | | acidity | | | total acidity contrib, % | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Ct | [HA] | [A$^-$] | Ct | [HA] | [A$^-$] | Ct | [H$_2$CO] | [HCO$_3$] | [H$^+$] | mineral (eq 4) | total (eq 5) | formic | acetic |
| NG1 | 4.72 | 3.5 | 0.3 | 3.2 | 2.1 | 1.1 | 1.0 | 10 | 9.8 | 0.3 | 19.1 | 14.6 | 40.3 | 0.8 | 2.7 |
| NG2 | 4.67 | 3.5 | 0.4 | 3.1 | 2.0 | 1.1 | 0.9 | 10 | 9.8 | 0.2 | 21.4 | 17.1 | 42.7 | 0.9 | 2.6 |
| NG3 | 4.62 | 1.5 | 0.2 | 1.3 | 1.8 | 1.0 | 0.8 | 10 | 9.8 | 0.2 | 24.0 | 21.7 | 45.0 | 0.4 | 2.3 |
| G1 | 4.41 | 9.0 | 1.6 | 7.4 | 4.8 | 3.3 | 1.5 | 10 | 9.9 | 0.1 | 38.9 | 29.9 | 63.7 | 2.5 | 5.2 |
| G2 | 4.51 | 7.3 | 1.1 | 6.2 | 3.5 | 2.2 | 1.3 | 10 | 9.9 | 0.2 | 30.9 | 23.3 | 54.1 | 2.0 | 4.1 |
| G3 | 4.38 | 12.8 | 2.4 | 10.4 | 4.2 | 3.0 | 1.2 | 10 | 9.9 | 0.1 | 41.7 | 30.0 | 67.0 | 3.6 | 4.4 |
| all | 4.49 | 7.4 | 1.1 | 6.3 | 3.6 | 2.3 | 1.3 | 10 | 9.9 | 0.2 | 32.4 | 24.7 | 55.7 | 2.0 | 4.2 |

[a] All concentrations in microequivalents per liter.