FINGERPRINTING DIOXINS/FURANS IN SUSPENDED SOLIDS FROM AMBIENT WATERS AND WASTEWATER DISCHARGES IN NEW YORK/NEW JERSEY HARBOR AND THE HUDSON RIVER

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Introduction

Dioxins and furans occur in New York Harbor sediments and biota at levels potentially harmful to wildlife and to humans consuming wildlife [1]. Field pre-concentration coupled with HRGC/HRMS lab methods achieve quantification of seven PCDDs and ten PCDFs on suspended particulates in water samples. Water column data permits comparison with water quality standards, calculation of loads, and elucidation of fingerprints helpful in identifying sources.

Methods and Materials

Large volume samples (200 L to 5,000L) from ambient waters, tributaries, and finished wastewaters from municipal sewage treatment plants were pumped through 1 micron glass fiber filter cartridges. Soxhlet extracts from suspended solids were analyzed for the seventeen 2,3,7,8-substituted dioxins and furans. Field concentration coupled with isotopic dilution HRGC/HRMS techniques (USEPA Method 1613B) allows quantification of dioxin and dioxin-like compounds. Utilization of TEFs normalizes substances having large differences in concentration and summarizes these concentrations into a single TEQ parameter.

Sampling sites were categorized as:

a) tributaries to the Hudson, (Tribs), 6 sites, 12 samples
b) "ambient-clean", areas outside of the harbor, (Amb-clean), 4 sites, 13 samples
c) "ambient-dirty", the heart of the harbor, (Amb-dirty), 11 sites, 32 samples
d) main stem of the Hudson River, (Hudson), 5 sites, 14 samples and
e) final effluent from sewage treatment plants, (STPs), 16 sites, 27 samples.

Results and Discussion

Average dioxin/furan TEQs by sample type show that treated wastewaters are not significantly more contaminated than ambient waters in the harbor.

Table 1 Mean dioxin/furan concentration in pg/L TEQ

source type	Amb-clean	STP	Tribs	Hudson	Amb-dirty
pg/L TEQ	0.06	0.16	0.25	0.72	3.1

The highest concentrations occurred in New Jersey's Passaic/Hackensack/Newark Bay area (5.6 pg/L TEQ). New York State's ambient water quality standard for TEQ dioxin is 0.0006 pg/L [2]. Each of the 101 samples has a pattern of congener abundances. Eight congeners or congener clusters were converted to TEQs by multiplication by the NATO TEFs. The eight were 2,3,7,8-TCDD; 1,2,3,7,8-PeCDD; the cluster 1,2,3,6,7,8-HxCDD plus 1,2,3,7,8,9-HxCDD plus 1,2,3,4,6,7,8-HpCDD; OCDD; 2,3,7,8-TCDF; 2,3,4,7,8-PeCDF; the cluster 1,2,3,4,7,8-HxCDF plus 1,2,3,6,7,8-HxCDF; and 1,2,3,4,6,7,8-HpCDF. On average, these congeners account for 97% of the total dioxin/furan TEQ. The minimum was 90% of the TEQ. Differences between the relative abundances of the TEQ converted congeners were determined by Euclidean distance *d* where:

$d = ((a_1 - a_2)^2 + (b_1-b_2)^2 + \ldots (n_1-n_2)^2)^{0.5}$ and

where a_1 is the a^{th} congener from sample 1 and so forth [3].

There are 5,050 differences between 101 observations. Table 2 shows the average, (and standard deviation) of differences between TEQ patterns from 65 or more comparisons.

Table 2. Average (and std dev) TEQ Euclidean distances between sample type.

	Amb-dirty	Amb-clean	Hudson	STP	Trib
Amb-dirty	0.34 (0.22)				
Amb-clean	0.38 (0.19)	0.21 (0.08)			
Hudson	0.47 (0.24)	0.25 (0.09)	0.17 (0.08)		
STP	0.55 (0.23)	0.36 (0.12)	0.29 (0.09)	0.26 (0.12)	
Trib	0.53 (0.23)	0.33 (0.10)	0.23 (0.08)	0.26 (0.10)	0.18 (0.10)

Samples taken from the Hudson River are most similar in congener pattern to each other. The "Amb-dirty" samples were, as a whole, most dissimilar. The greatest difference between types was between "Amb-dirty" and STPs. Since multiple samples were taken at each site, within site comparisons are possible (Table 3).

Table 3. Average (and std dev) Euclidean distances within sites by sample type.

source-type	Amb-dirty	Amb-clean	Hudson	STP	Tribs
difference (std dev)	0.15 (0.08)	0.20 (0.05)	0.12 (0.05)	0.26 (0.08)	0.13 (0.05)

Average differences between samples taken at the same site are less than those between samples from different sites of the same source-type with the exception of samples from STPs. Sources of dioxins/furans within a STP are as variable as those between STPs. There is no discernable STP dioxin/furan fingerprint.

The case of the Passaic and Arthur Kill Rivers (Figure 1) illustrates TEQ fingerprinting. Dioxin/furan abundances in the tidal Passaic is dominated by a single congener, 2,3,7,8-TCDD, where it constitutes as much as 90% of the total TEQ. The lower Passaic River is highly industrialized with a long history of dye and pesticide manufacturing. This includes a facility that manufactured 2,4,5-trichlorophenoxy acetic acid for Agent Orange [4]. In the Arthur Kill, 14 km to the south, 2,3,7,8-TCDD is still the single largest contributor to TEQ but other congeners,

particularly 2,3,4,7,8-PeCDF, are becoming more important. Dioxin trackdown should then identify sources of the other congeners. Effluent from a treatment plant processing leachate from a large landfill showed low dioxin concentrations (0.4 pg/L – less than Arthur Kill ambient water level). A source of 2,3,4,7,8-PeCDF was seen in a tidal stream, Mill Creek. This stream is affected by a facility incinerating obsolete electrical equipment. In terms of Euclidean distance, the difference between the Passaic and Mill Creek is 0.96; between the Passaic and the Arthur Kill is 0.43, and between Mill Creek and its receiving body, the Arthur Kill is 0.56. The large difference between Mill Creek and the Arthur Kill suggests that the material in Mill Creek is not just tidal wash but represents a distinct dioxin source (Figure 2).

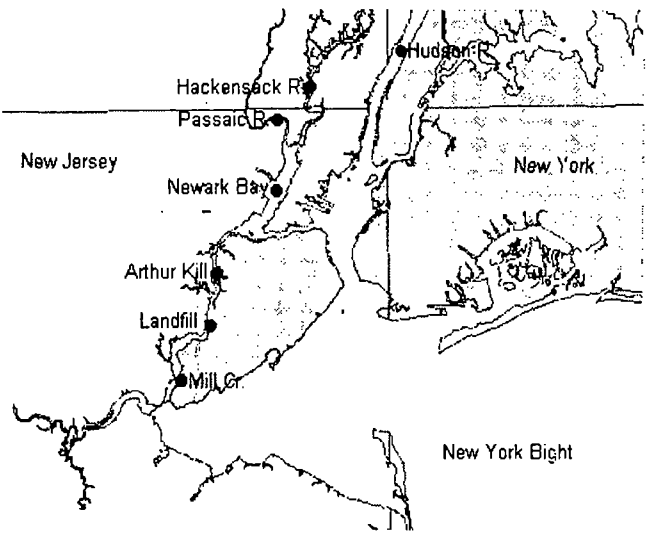

Figure 1. New York/New Jersey Harbor.

There is no thorough inventory of dioxin sources to the Arthur Kill but Mill Creek does supply a relatively rich source of 2,3,4,7,8-PeCDF. In New York Harbor some old industrial sites appear to be more important dioxin sources that the STPs. Loadings from the treatment plants are calculable but the old industrial sites are affecting tidal waters where loadings are not readily obtained. Evidence from fingerprints suggests dioxins/furans in the ambient waters of the harbor are more similar to patterns seen in the industrial sites than from the wastewater treatment plant effluents.

Trackdown of dioxin sources requires consistent detection of all congeners. This objective was largely met where 2,3,7,8-TCDD was not quantitated in only 16% of the samples. Source identification requires both quantitative data and qualitative information about fingerprints. Euclidean distances permits the quantification of fingerprints and allows large data sets to be evaluated more efficiently than by examining individual graphic images.

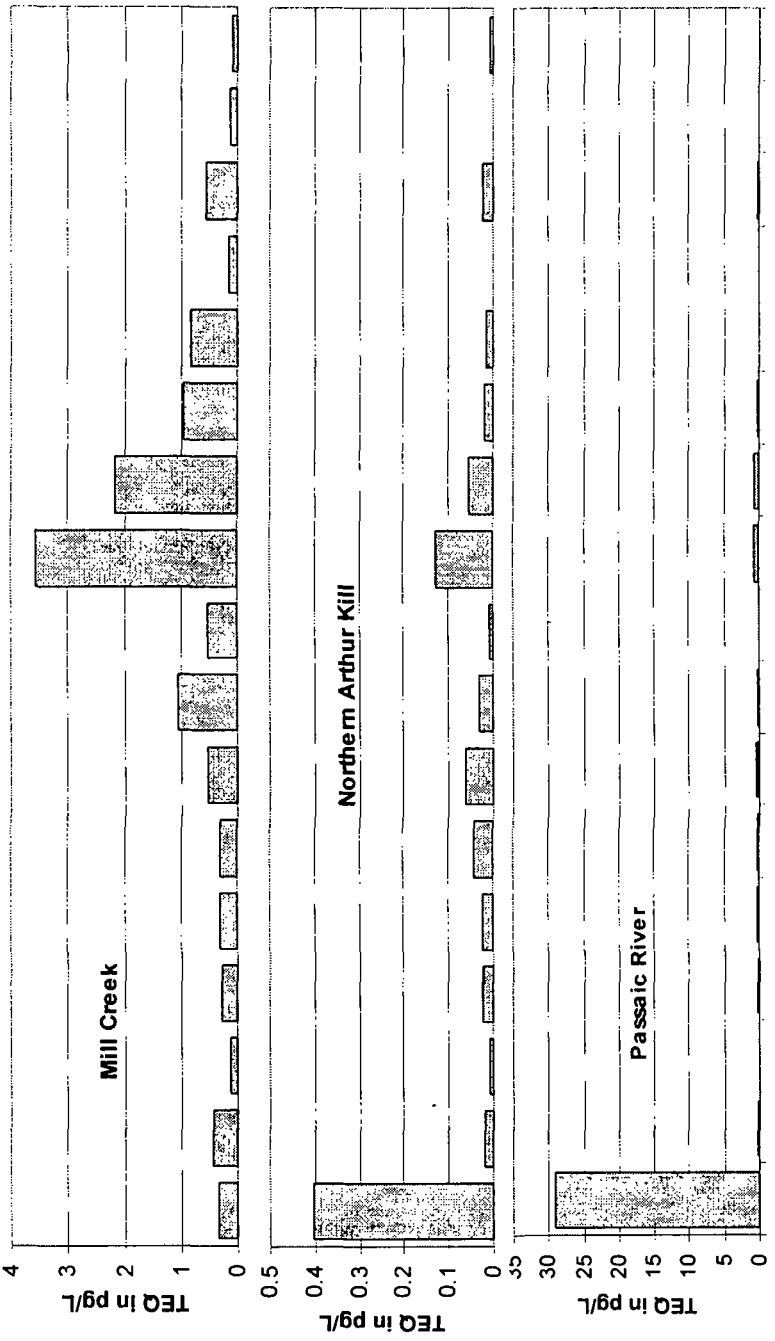

Figure 2. Filterable solids data; Mill Creek (top), 12.4 pg/L TEQ; Northern Arthur Kill (middle) 0.88 pg/L TEQ; and Passaic River (bottom), 32.5 pg/L TEQ.

Acknowledgements

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