DETERMINATION OF PCDD/PCDF AND 209 PCB CONGENERS IN NEW YORK HARBOR AND HUDSON BASIN USING FILTRATION/XAD INTEGRATING SAMPLERS AND US EPA METHODS 1668 AND 1613B

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Introduction

As part of an extensive program to assess and eliminate contaminant sources to New York Harbor, concentrations of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) and polychlorinated biphenyl (PCB) congeners were determined in a variety of effluent waste streams and surface waters. Using a combination of large volume water samples and high sensitivity HRGC/HRMS analytical methods, concentrations of PCDD/PCDFs and PCB congeners in surface waters were determined to low parts per quintillion levels (femtogram/L). Sample concentrations of PCDD/PCDFs were determined using EPA method 1613B[1] and corresponding sample concentrations of PCBs using a modified full congener version of EPA Method 1668[2]. In this paper, we present data on the significance of the co-planar PCBs[3] to total toxic equivalents (TEQ) and suggest the advantages of conducting a full scan for all the PCB congeners.

Materials and Methods

Water samples were collected using an extraction system called TOPS (Trace Organics Platform Sampler) consisting of a filter (nominal one-micron porosity glass fiber cartridge filter) and XAD resin. The system is totally enclosed and operated in the field where the potential sample size is unlimited. Extraction of PCDD/PCDFs and PCBs was by soxhlet with dichloromethane or 80/20 toluene/acetone for XAD resin column or cartridge filters and the extract split for various analyses. A variety of appropriate clean-up steps on different chromatography columns allowed analysis from a final volume of 20 or 100μL.

These extracts were analyzed for 209 PCB congeners using a modified form of US EPA Method 1668 [2]. Analysis procedures for PCDDs and PCDFs were in accordance with US EPA Method 1613B[1] for the determination of tetra- through octa-chlorinated, 2,3,7,8-substituted PCDDs and PCDFs.

Instrumental analysis was conducted according to Methods 1613B and 1668 using either a VG 70-VSE or Autospec Ultima magnetic sector high resolution MS equipped with an HP 5890/6890 gas chromatograph and an Alpha data system running Opus software. PCB and PCDD/PCDF analyses were conducted using SPB-Octyl and DB-5 chromatography columns, respectively. 2,3,7,8- tetrachlorodibenzofuran (TCDF) was confirmed as per the method. Initial calibration was

achieved by analysis of five calibration standards. Additionally, for PCB analysis, a 209 congener calibration standard was analyzed. Sample concentrations were determined over the linear range of the calibration series and down to the sample specific detection limit (SDL) for each analyte.

Results and Discussion

Seven 2,3,7,8-substituted PCDDs, ten 2,3,7,8-substituted PCDFs, and 15 co-planar PCBs were normalized by multiplying their measured concentrations by the appropriate NATO or WHO toxicity-equivalence factors (TEFs). The summation of these products yields a TEQ, which expresses these analyte concentrations as a single number, equivalent to that of a toxicity derived exclusively from 2,3,7,8-tetrachlorodioxin (TCDD). In 25 cases, there are data sets available for PCBs from filters and XAD and for PCDD/PCDFs from filters. Figure 1 shows that in many cases both in surface and treated wastewaters, PCBs are significant contributors to the total TEQ. In a few cases, a single PCB congener, IUPAC 126 (3,3',4,4',5-PeCB) was found to be the largest source of TEQ due in large part to its high TEF – 0.1. The literature[4] indicates that IUPAC 126 is a very minor constituent of Aroclors (<0.05%) and a minor congener in some Clophens (0.46% of A60). In our NY Harbor data, IUPAC 126 had an average abundance of 0.01%. However, the sample with a total TEQ of 2030 fg/L got 88% of its TEQ from PCBs and got 71% of its TEQ from IUPAC 126 in particular. In this sample, IUPAC 126 was 0.12% of the total PCB concentration. The sample with the greatest TEQ in this set showed very little contribution to the TEQ from PCBs. It came from waters affected by the manufacture of 2,4,5-trichlorophenoxy acetic acid. This was a component used in the formulation of the Vietnam War era herbicide, Agent Orange, whose production process yielded a waste rich in 2,3,7,8-TCDD.

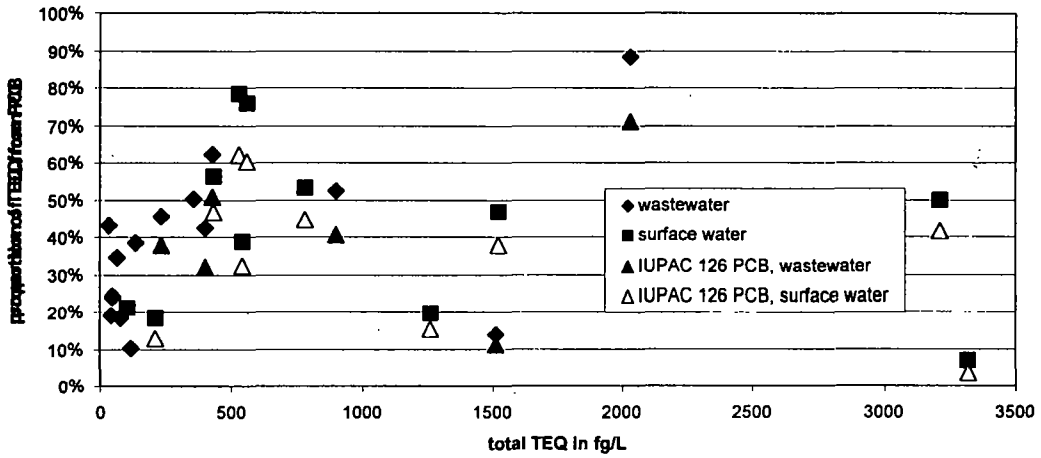

Figure 1. Range of TEQ values and contribution to these values by co-planar PCBs.

Among the individual PCB congeners resolved by the modified Method 1668 is IUPAC 11 (3,3'-DiCB). Identification of IUPAC 11 was confirmed by examining three samples using low resolution open-scan GC/MS. The fragmentation patterns observed exactly matched those of

dichlorobiphenyl and the elution time matched that of the 3,3'- isomer. While the literature indicates that IUPAC 11 is present at less than 0.05% in Aroclors[4], the median ambient dissolved phase ratio (from XAD) was 2.4% and its median solid phase (from filters) was 0.58%. Ratios from final treated wastewater were similar – 1.8% from XAD and 0.99% from filters. However, three wastewater sites show IUPAC 11 to constitute from 50 to 92% of the total dissolved (XAD) PCBs. The sample with 92% IUPAC 11 had a total of 32 ng/L dissolved (XAD) PCB. The NYS Water Quality Standard (WQS) for PCB (for human consumption of fish) is 0.001 ng/L.

IUPAC 11 has been associated with 3,3'-dichlorobenzidine salts which are intermediates in the manufacture of dry phthalocyanine blue, phthalocyanine green, and diarylide yellow pigments[5]. Phthalocyanine blue and green are used for rubber, plastics, inks, paints, coatings, and floor coverings. Phthalocyanine blue (called "phthalo blue") is commonly used for cyan and diarylide yellow is used for yellow in newspaper printing[6,7].

3,3'-Dichlorobenzidine is also used as a compounding ingredient for rubber and plastics, and can be used to test for the presence of gold. It is used in the formulation of the raw material tetraminobiphenyl which is used to produce polybenzimidazole (PBI), used in many protective clothing applications, such as firefighters' apparel, welders' garments, high temperature gloves, and crash rescue garments[8,9].

A working hypothesis is that IUPAC 11 originates from a commonly used item, perhaps printing ink, and is seen in greater abundances from sites where the base material is manufactured, handled, or spilled.

One other observation is that the site showing the maximum concentration of IUPAC 11 was also the site showing the maximum concentration of IUPAC 126. Whether these results are related or are merely a coincidence of separate events in the same service area is as yet unknown.

The NYS WQS for PCDD/PCDF uses only 17 dioxin and furan congeners. However, if the TEFs for the PCDD/PCDFs and PCBs are indeed comparable, this work suggests that complete characterization of TEQ values requires the measurement of the co-planar PCBs in general and IUPAC 126 in particular. Aroclors may not be the only source of environmentally distributed PCBs.

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