ANALYSIS OF PERSISTENT ORGANIC POLLUTANTS IN THE NEWARK BAY ESTUARY, NEW JERSEY, U.S.A

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Introduction

As part of an ongoing effort for harbor restoration, a large-scale study has been initiated to determine the sources and magnitudes of contaminants and sediment entering the Newark Bay and Hudson River estuary system. The research is funded by the New Jersey Department of Environmental Protection, and is being conducted by the U.S Geological Survey-NJ, Stevens Institute of Technology, Stevens/Rutgers University, and the New Jersey Harbor Dischargers Group. The data collected will be used to model sediment and contaminant transport through the harbor system and to support resource management policy. A sampling and analytical program was developed to accurately measure inputs of contaminants and sediment from the major tributaries and point sources. Contaminants in both the aqueous (dissolved) and the suspended sediment phases were analyzed for trace level organics, trace metals, carbon, and suspended solids. This paper describes the analytical program for the organic contaminants.

To measure concentrations of trace level organochlorines and polyaromatic hydrocarbons (PAHs), large volume (>50 Liter) samples are being collected for analysis. Similar sampling methods have been used by the Great Lakes National Program Office of the USEPA, working in conjunction with the Battelle Pacific Northwest National Laboratory[1] and the San Francisco Estuary Institute.[2] The New York State Department of Environmental Conservation (NYSDEC) Analytical Service Protocol [3]extends these techniques by including more compound classes and by making greater use of isotope dilution quantification, selected ion monitoring (SIM), and high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS). The analytical program described herein adapts the previous work to meet the NJ program objectives. The application of high-volume sampling and high-specificity analytical techniques produces detection limits up to 4 orders of magnitude lower than those available using EPA regulatory methods.

Sample Matrices and Media

The sampling methods are designed to capture suspended sediments on glass fiber filters (GFFs) and dissolved compounds on XAD resin. Targeted minimum sample amounts are 5 grams of sediment collected on filters and 50L passed through the XAD columns. Water is filtered in the field through a 0.5 micron (μ) canister and flat filter (GF/F 0.7μ pore size), before being passed through two resin columns, each containing 55 grams of precleaned XAD-2 resin. The first column is spiked with a solution of 13C-labeled field surrogates. Flow rates of 2L/min through the cartridge filter and 200mL/min through the XAD columns are used. The two filters are combined for particulate phase analysis, and the 2 columns are combined for the dissolved phase. The phase separation is operationally defined, since fine solids, oils, and grease, are not

completely trapped by the filters. Unfiltered water (1 L) is collected for analysis of dissolved PAHs. These samples are filtered (0.7 μ GF/F filters) in the laboratory before extraction. The sediment collected by the large volume samplers is used for particulate PAH analysis.

Analytical Methods

Isotope dilution HRGC/HRMS is used to measure 107 polychlorinated biphenyl (PCB) congeners, based on guidance from EPA Method 1668.[4] An adaptation of EPA Method 1613B[5] is used to measure 17 polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/PCDFs). An isotope dilution HRGC/HRMS procedure is used to measure 27 organochlorine pesticides (OCPs). The procedure was developed by Severn Trent Laboratories (STL)-Knoxville in collaboration with Axys Analytical and NYSDEC staff. Isotope dilution HRGC/low-resolution (LR) MS is used for determining 24 PAHs. This method was developed by STL, and is based on the California Air Resources Board Method 429, with contributions by the NYSDEC Analytical Services Protocol and Philip Analytical Services staff.

Sample Preparation

The XAD cartridges are first weighed, any excess water drained into a separatory funnel, and then reweighed. The XAD resin, and the combined GFF filters, are transferred into separate pre-extracted Soxhlet-Dean/Stark extraction assemblies, and spiked with ^{13}C-labeled and deuterated analogs of the target compounds (internal standards). The resin and filters are extracted for 16 hours with 700 mL of acetone:hexane (1:1 v/v). The resin extract is then combined with the extract of the separatory funnel and then concentrated to 10 mL, which is split 50% for pesticide analysis, 30% for PCB analysis, 20% for PCDD/PCDF analysis (when required) or archived.

The acetone:hexane sediment (GFF) extract is removed. The GFFs are further extracted with 700 ml of toluene for 16 hours to extract residual PCDD/PCDF. A 25% aliquot of this extract is combined in a separatory funnel with a 25% aliquot of the acetone:hexane sediment extract. The sediment extract is then concentrated to 10 mL which is split 20% for PAH, 30% for pesticides, 20% for dioxin, 20% for PCB analysis, and 10% is archived. The labeled cleanup standards are then added to the extracts. Interferences are removed from PCDD/PCDF extracts by the application of an acid/base back extraction, followed by silica gel, alumina and carbon liquid chromatography. The PCB analysis extracts are cleaned using acid/base back extraction followed by Florisil® cleanup. The extracts are concentrated to volumes 20μL for dioxin and 100μL for PCB analysis. The PAH extracts are reduced to a final volume of 0.5 mL and, if necessary, cleaned up by gel permeation chromatography.

For pesticide analysis, the extract is first exchanged to hexane and then purified using a Florisil column. The extract is collected in two fractions, designated F1 (non-polar) and F2 (polar), that are then exchanged to nonane and concentrated to 200 μL. Aliquots of F1 and F2 extracts are then combined in equal amounts and the ^{13}C-labeled recovery standards are added. If ion-suppression is observed in the chromatographic data, then the uncombined F2 fraction is re-analyzed. Dissolved PAHs are measured by filtering grab samples, then spiking with deuterium-labeled analogs (Table 1) and extracting for 18 hours in a continuous liquid-liquid extractor using 450mL of methylene chloride. The extract is then concentrated in a Kuderna-Danish concentration flask to 10 mL, and further concentrated to 0.5 mL.

GC/MS Analysis

All PCDD/PCDF, PCB, OCP analysis is performed by HRGC/HRMS operating at >10,000 resolving power in the selected ion monitoring mode, using a Hewlett-Packard® 6890-Finnigan/MAT MAT95S instrument system. A 30m SPB-Octyl® fused silica column is used for PCB analysis and a 60m RTX-5® fused silica capillary column is used for PCDD/PCDF and OCP analysis. The HRGC/LRMS PAH analysis is performed using a Hewlett-Packard® 6890 GC/5973 MSD with a 30m XTI-MS® fused silica capillary column. The instrument is tuned to meet EPA Method 8270C DFTPP ion abundance criteria.

An elution order verification study was initiated before the initial calibration and will be repeated during the study due to the possibility that the PCB elution order may change over time or vary between SPB-Octyl columns. Forty-seven solutions, each containing 3 to 6 individual PCB congeners, were prepared from certified, individual stocks. The congeners selected for each mix are separated by 3 or more minutes from the nearest eluting congeners in the mixture. The 19 ^{13}C-labeled analogs were added to each test solution to provide relative retention time references. This data set, when reproduced over time and on several columns, will help in designing a test solution that is predictive of changes in column phase polarity and elution order.

For the PCDD/PCDFs and PAHs, the native compounds are referenced to their respective labeled analog standards, which are referenced to the respective labeled pre-injection (recovery) standards. For OCPs and PCBs, a lower percentage of labeled analogs are commercially available. For the OCPs, the pre-extraction standard that most closely resembles, or demonstrates analytical covariance with the native compound, is used for standardization, and a 6-point calibration series is used to demonstrate linearity. A mid-point calibration solution brackets each 12-hour period, and the average response factor of the bracketing standards is used for sample quantifications. For the PCBs, 19 native compounds spanning the homolog series are standardized to their labeled analogs, using the mean response from a 5-point calibration. For the remaining PCB congeners, a response factor is calculated from a single point concentration of a commercially prepared 209 mixture. Daily linearity checks are made of the 19 compounds using a midpoint standard. If this standard does not fall within limits, both the 19 and 209 congeners calibration solutions are re-analyzed and new response factors are calculated.

Samples from fresh water (head of tide), estuarine (saline) water, and treated waste effluent have been analyzed by these procedures. The results are presented in another abstract submitted for inclusion in this year's conference[6]. The precision in the analysis of co-located samples in this preliminary work is encouraging. The effluent samples were the most challenging due to interferences from color, turbidity, viscosity, and the tendency to form emulsions. As a result, a more complex suite of cleanups was chosen than those used for the other matrices. Internal standard recoveries for all analyses were within traditionally acceptable recovery ranges, with few exceptions. One such exception occurred in the OCP analysis. The polar pesticide, endosulfan-1-d4 has so far proved significantly more variable than the other internal standards. The recoveries of native endosulfan sulfate and endosulfan 2 were also problematic. The addition of more predictive labeled internal standards and the use of less active surfaces in the fractionation and analysis steps are being attempted to help alleviate these problems.

A program has been designed to help ensure consistent quality of the data. This includes analysis of four types of standard reference material (SRM) samples for each event. These SRMs are produced using NIST solutions or sediment, and include: SRM#1: a low level calibration check for all compounds, at a concentration of the lowest calibration standard, SRM#2: the recovery of SRM #1 solution from XAD column to evaluate the efficiency of the method for PCBs and OCPs, SRM #3: extraction of a sediment spiked with a PCDD standard, and SRM #4: extraction of water spiked with a standard PAH solution. Other steps include participation in the NIST/NOAA program, the routine analysis of the 209 PCB calibration standard solution, checking the cleanliness of XAD and GFF filters before use, and standard laboratory quality control practices.

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