Contaminant Assessment and Reduction Project (CARP)

Toxic Chemicals in New York Harbor and Vicinity - Design of the Trace Organics Platform Sampler (TOPS).

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ABSTRACT

The New York State Department of Environmental Conservation developed the Trace Organics Platform Sampler (TOPS) to measure field concentrations of dilute organic pollutants. By moving extraction operations from the lab (where sample volume is limited) to the field (where it is unlimited), TOPS allows for trace level determination of PCBs, dioxins, and persistent organochlorine compounds. TOPS pumps water from a sampling source through a glass fiber filter cartridge to collect suspended solids. Some filtered water is wasted, and the remainder is pulled through column(s) of XAD-2 resin. Flow totalizers record the volumes of water wasted and water passing through the XAD. The use of two pumps in the TOPS ensures detection of chemicals associated with suspended solids while not subjecting the XAD to excessive flow rates.

TOPS is generally operated manually in the lab or at sewage-treatment plants, but has been adapted to run automatically and from ships. Automatic operation at remote USGS stream gages is done with data loggers, which integrate river-stage measurements and TOPS operation. At a critical river stage (and discharge), TOPS operation is triggered and runs at intervals proportional to river discharge. Maritime sampling is done with a tow-fish deployed off ships' sides, away from ship-generated pollutants, while the ship slowly cruises around an area to obtain temporal and spatial integration. TOPS has a great deal of flexibility in operation for differing needs, and samples for additional constituents are readily taken from side chain assemblies.

INTRODUCTION

The New York State Department of Environmental Conservation (NYSDEC) is attempting to reduce toxic chemicals in New York Harbor. This work is being done under the Contamination Assessment and Reduction Project (CARP). Authority for the state's participation falls from the NY/NJ Harbor Estuary Program (HEP) and the Comprehensive Conservation and Management Plan (CCMP). The Bi-State Dredging Agreement, signed by the Governors of New York and New Jersey in 1996 states in part:

"The States commit to implementation of the Harbor Estuary plan as it relates to the study of sediment contaminants, the identification and elimination of the sources of contamination of harbor sediments, the remediation of contaminated areas, and the pursuit and sanction of polluting entities".

The studies reported here are partially supported by funds from the Port Authority of New York/New Jersey. Trackdown support comes in part from the USEPA for work in the Kills, and in part from the Hudson Estuary Program for work in the Wallkill River and lower Hudson. Technical oversight comes from the CARP Work Group - a group of government, academic, and consultant experts.

NYSDEC is simultaneously undertaking a variety of projects including studies of sediments, biota, and trackdown of contaminant sources in surface and wastewaters. The major objectives of the sampling are:

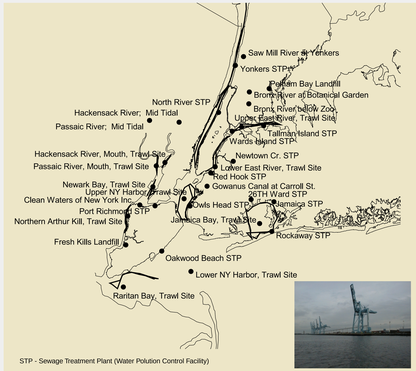
- **Develop data to assist in the identification and remediation of continuing sources of toxics contamination to the harbor ("trackdown");**
- **Develop data to assist in developing mathematical models designed to predict when sediments and biota will attain certain qualities;**
- **Develop information of use in setting total maximum daily loads (TMDLs); and**
- **Develop data potentially useable in pursuing environmental quality damage litigation.**

Here, we will discuss preliminary data developed by the water program. The water program consists of five elements:

- **Ambient measurements to determine concentrations of the target chemicals at nineteen tidal sites extending from the mid-Hudson to boundary sites well out into the New York Bight and Long Island Sound. These 19 sites are visited once per season. One ambient station, Hudson River at Poughkeepsie, is a fixed, event-triggered site to be sampled 12 times;**
- **Point Source measurements of contaminant loadings from eighteen final effluents at water pollution control facilities (WPCFs), three minor tributaries, three industrial sites, eight combined sewer overflow sites (CSOs), two storm water overflow (SWO) and five landfill leachate sites;**
- **Tributary loading measurements from the upper Hudson, the Mohawk, and the Wallkill Rivers;**
- **Surface water trackdown studies at sites in the Kills, East River, lower Hudson, and Wallkill River; and**
- **Wastewater trackdown studies in the service areas of selected New York City WPCFs.**

Parallel efforts are being undertaken in New Jersey include tributary, ambient, trackdown, and point source load sampling. The New Jersey program uses a similar analyte list and follows comparable sampling methods.

At this time, sampling is still underway and some of the critical source categories have yet to be visited. Much of the work already accomplished has not emerged from the analytical labs. Nevertheless, the available data may indicate directions to pursue. For example we can now focus trackdown efforts on a limited number of areas and on a limited number of analytes.



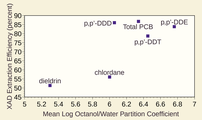
STP - Sewage Treatment Plant (Water Polution Control Facility)

CARP Sample Sites

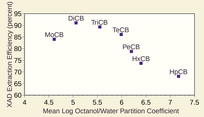
Abbreviation	Site Name	Sample type
26WSTP	26th Ward WPCF	Water Polution Control Facility
BBSTP	Bowery Bay WPCF	Water Polution Control Facility
BIGHT	New York Bight, Trawl Site	Ambient
BIGHT-D	New York Bight, Trawl Site, December 1998	Ambient
BRBG	River at Botanical Garden	Tributary
BRBZ	Bronx River below Zoo	Tributary
CISTP	Cony Island WPCF	Water Polution Control Facility
CWNY	Clean Waters of New York	Industrial Effluent
GOWC	Gowanus Canal (Carroll St).	Tributary
HPSTP	Hunts Point WPCF	Water Polution Control Facility
HRHAV	Hudson River, Haverstraw Bay, Trawl Site	Ambient
HRKP	Mid-Hudson Trawl Site	Ambient
HRMM	Hackensack River, Mouth, Trawl Site	Ambient
HRMT	Hackensack River, Mid-Tidal	Ambient
HRPOU	Hudson River at Poughkeepsie	Ambient
HRSHAR	Hudson River below Harlem River, Trawl Site	Ambient
HRTZHA	Hudson River, Tappen Zee to Harlem R., Trawl Site	Ambient
HRWA	Hudson River, Waterford	Tributary
JAMB	Jamaica Bay, Trawl Site	Ambient
JASTP	Jamaica WPCF	Water Polution Control Facility
LER	Lower East River, Trawl Site	Ambient
LISE	Long Island Sound, Eaton's Neck to Stamford, Trawl Site	Ambient
LISJ	Long Island Sound, Port Jefferson, Trawl Site	Ambient
LOWB	Lower New York Bay, Trawl Site	Ambient
MORCO	Mohawk River, Cohoes	Tributary
NAK	Northern Arthur Kill, Trawl Site	Ambient
NEWB	Newark Bay, Trawl Site	Ambient
NRSTP	North River, WPCF	Water Polution Control Facility
NTSTP	Newtown Creek, WPCF	Water Polution Control Facility
OBSTP	Oakwood Beach, WPCF	Water Polution Control Facility
OHSTP	Owls Head WPCF	Water Polution Control Facility
PBLF	Pelham Bay Landfill Holding Tank	Landfill
PRMB	Passaic River, Mouth, Bottom	Ambient
PRMS	Passaic River, Mouth, Surface, Trawl Site	Ambient
PRMT	Passaic River, Mid-Tidal	Ambient
PRSTP	Port Richmond, WPCF	Water Polution Control Facility
PVSC	Passaic Valley Sewage Authority	Influent - WPCF
RARB	Raritan Bay, Trawl Site	Ambient
RENSTP	Rensselaer WPCF	Water Polution Control Facility
RHSTP	Red Hook WPCF	Water Polution Control Facility
ROCSTP	Rockland County WPCF	Water Polution Control Facility
ROSTP	Rockaway WPCF	Water Polution Control Facility
SMR	Saw Mill River, Yonkers	Tributary
TISTP	Tallman Island, WPCF	Water Polution Control Facility
UER	Upper East River, Trawl Site	Ambient
UPB	Upper NY Harbor, trawl Site	Ambient
WALLR	Wallkill River at New Paltz	Tributary
WISTP	Wards Island WPCF	Water Polution Control Facility

XAD Extraction Efficiency

Factors governing XAD extraction efficiency are complicated. A simple Kow model would argue that extraction efficiency improves with increasing hydrophobicity as measured by the log of the octanol/water partition coefficient (Kow). XAD is relatively successful extracting PCBs and the DDTs but has diminished success with chemicals having a Kow of 6 and less - such as chlordane and dieldrin.



A similar comparison with PCB homologues shows decreasing efficiencies with Kows greater than 5.5



Remote TOPS Operation

The start of sampling events are based on critical changes in stage over time at a USGS stream gaging station upstream of the sampling station. Manual triggering (by phone) is also possible to sample over a fixed length of time (see plots of 2 week sample below).

Once sampling is initiated the volume of water passing the stream gaging station is calculated by a data logger and calls are made to a data logger at the downstream sampling shelter each time X cubic feet of water pass the gaging station. An event usually entails several hundred calls between data loggers/shelters.

The sampling station data logger operates the TOPS based on the timing of calls from the stream gaging data logger. The TOPS is run following each call until a fixed volume of water is pumped through both the filter and XAD.

Dissolved PAH samples are collected with one of the automatic pumping samplers as a sub-sample of the number of times the TOPS turns on and off.

Sediment and TOC samples are collected over the storm hydrograph based on changes in stage and time between samples.

Sampling continues until the the stage falls to 80% of the difference between the event start and peak or until manually terminated.

Trace Organic Platform Sampler (TOPS)

One of the fundamental goals of CARP is consistent detection of all target chemicals from all media. Satisfaction of this requirement will permit calculation of loads (mass/time) for the target chemicals. Some of the target chemicals are expected to be at concentrations below detection by conventional sampling methods.

Detection of trace organic chemicals in the water column has been, in the past, very problematic. Much of the regulatory data-base is filled with "non-detections" - evidences of failure in either or both field work or laboratory analysis to measure ubiquitously occurring substances at environmentally relevant concentrations. In order to meet the goals of CARP, the NYSDEC selected the Trace Organics Platform Sampler (TOPS) as its principal tool for obtaining water column samples. TOPS is a set of plumbing, pumps, and sensors that concentrates hydrophobic organic chemicals from surface waters. TOPS uses glass fiber cartridge filters to capture suspended solids (1 µm pore size) and the synthetic resin Amberlite XAD-2 (XAD) to capture dissolved-phase hydrophobic substances. Practically, XAD is usually insufficient for recovery of truly dissolved dioxins and furans and as XAD ages, it releases naphthalenes making it questionable for PAH sampling. Consequently, XAD is used infrequently for the dioxins and furans and not at all for aqueous phase PAHs. Aqueous PAHs are sampled separately by simple grabs. Work in New York Harbor with this system was begun in the fall of 1997 and began in earnest in the fall of 1998.

One µm pore size filters were chosen because they are readily available in desirable configurations (glass fiber, stainless steel mandrel, four inch length) and because they were assumed to be efficient at capturing most of the solids in most environments.

XAD is a non-ionic polymeric adsorbent of hydrophobic cross-linked polystyrene copolymer supplied as 20-60 mesh beads. The beads are an agglomeration of many microspheres giving a continuous gel phase and a continuous pore phase. XAD surface area is 300 m^2/g. The open cell porous structure allows water to easily penetrate pores. In the adsorption process, the hydrophobic portion of the adsorbate molecule is preferentially adsorbed on the hydrophobic polystyrene surface of the resin while the hydrophilic section of the adsorbate remains oriented in the aqueous phase. Compounds adsorbed do not penetrate into the microsphere phase and remain at the surface where they can be easily eluted. The selectivity and extent of adsorption of soluble organic compounds by XAD increases as the hydrophobicity of the adsorbate molecule increases. For example , p,p'-DDT (Kow = 6.058) is extracted more efficiently than dieldrin (Kow = 5.299).

The best use of TOPS is for obtaining whole water concentrations of highly dilute hydrophobic organic chemicals from ambient water. With adequate support, TOPS is a powerful field tool for deployment from ships or fixed locations where sample size is unlimited. In such cases, there is virtually no detection limit as more analyte is obtainable by simply pumping more water. In open water situations we now typically process over 5,000 L to ensure detection of all organic analytes.

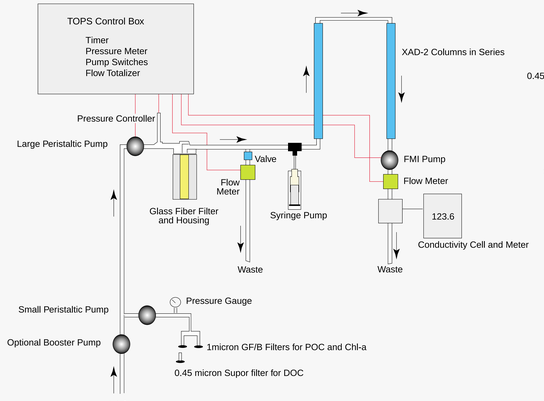
Where field set-up is inconvenient and concentrations are expected to be relatively high, TOPS can also be used in a bench-top mode. Samples on the order of tens of liters may be brought in from the field and batch-processed.

TOPS shipboard operation

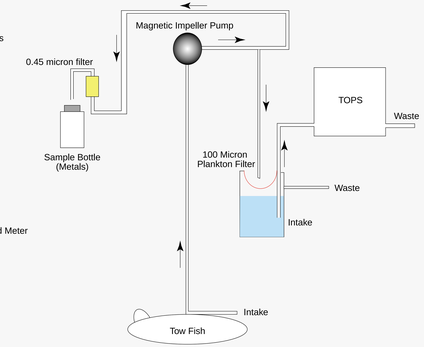
Towfish setup

Metered surrogates for quality control

TOPS Schematic



TOPS Shipboard Operation



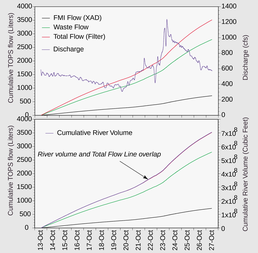
USGS

science for a changing world

As part of CARP, the U.S. Geological Survey (USGS) operates TOPS in New York at three sites on rivers tributary to the tidal Hudson River (Mohawk River at Cohoes, Wallkill River at New Paltz, and Hudson River at Waterford) and one tidal site on the Hudson (at Poughkeepsie). USGS has modified the TOPS to be operated and monitored remotely with data loggers to sample storm water runoff efficiently. TOPS sampling can be initiated manually by phone or automatically based on changes in river stage.

TOPS samples at tributary sites are collected on a flow-weighted basis. Because the TOPS composites water over a period during which stream flow is changing, the mass of contaminants needs to be sampled in proportion to the volume of water passing the sampling station to avoid bias in contaminant load calculations.

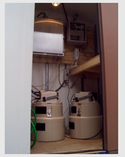
Additional automatic pumping samplers are used in the sampling shelter to collect samples for analysis of suspended sediment, total organic carbon (dissolved and suspended), and dissolved PAHs.



Flow weighted TOPS sampling on the Wallkill River during a recent 2 week sampling event. The amount of water sampled by the TOPS is directly proportional to the amount of river water passing the sampling station.

USGS Sampling shelter - Mohawk River at Cohoes

Data logger used to control sampling operations and communications



Interior of sampling shelter - TOPS and TOPS control box mounted to back wall. Automatic pumping samplers used for suspended sediment, organic carbon and dissolved PAHs are on floor