

# 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 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 citical river stage (and discharge), TOPS operation is triggered and runs at intervals proportional to river discharge. Maitime sampling is done with a tow-fish deployed off ships' sides, away from shipgenerated 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

#### 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 theWallkill Rivers;
- Surface water trackdown studies at sites in the Kills, East River, lower Hudson, andWallkill 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.

ຼ Saw Mill River ສັ∤ຯ້ອົກkers Fresh Kills Landfill

Trace Organic Platform Sampler (TOPS)

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

laboratory analysis to measure ubiquitously occurring substances at environmentally relevant concentrations

concentrates hydrophobic organic chemicals from surface waters. TOPS uses glass fiber cartridge filters to

dissolved-phase hydrophobic substances. Pactically, XAD is usually insufficient for recovery of truly dissolved

Aqueous PAHs are sampled separately by simple grabs. Work in New York Harbor with this system was begun

In order to meet the goals of CARP, the NYSDEC selected the Trace Organics Platform Sampler (TOPS) as its

One of the fundamental goals of CARP is consistent detection of all target chemicals from all media.

regulatory data-base is filled with "non-detections" - evidences of failure in either or both field work or

principal tool for obtaining water column samples. TOPS is a set of plumbing, pumps, and sensors that

capture suspended solids (1 µm pore size) and the synthetic resin Amberlite XAD-2 (XAD) to capture

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.

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

XAD is a non-ionic polymeric adsorbent of hydrophobic cross-linked polystyrene copolymer supplied as 20-60

continuous pore phase. XAD surface area is 300 m<sup>2</sup>/g. The open cell porous structure allows water to easily

penetrate pores. In the adsortion 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 penetate 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

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

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-

example, p,p'-DDT (Kow = 6.058) is extracted more efficiently than dieldrin (Kow = 5.299).

mesh beads. The beads are an agglomeration of many microspheres giving a continuous gel phase and a

STP - Sewage Treatment Plant (Water Polution Control Facility)

in the fall of 1997 and began in earnest in the fall of 1998.

over 5,000 L to ensure detection of all organic analytes.

processed.

most of the solids in most environments.

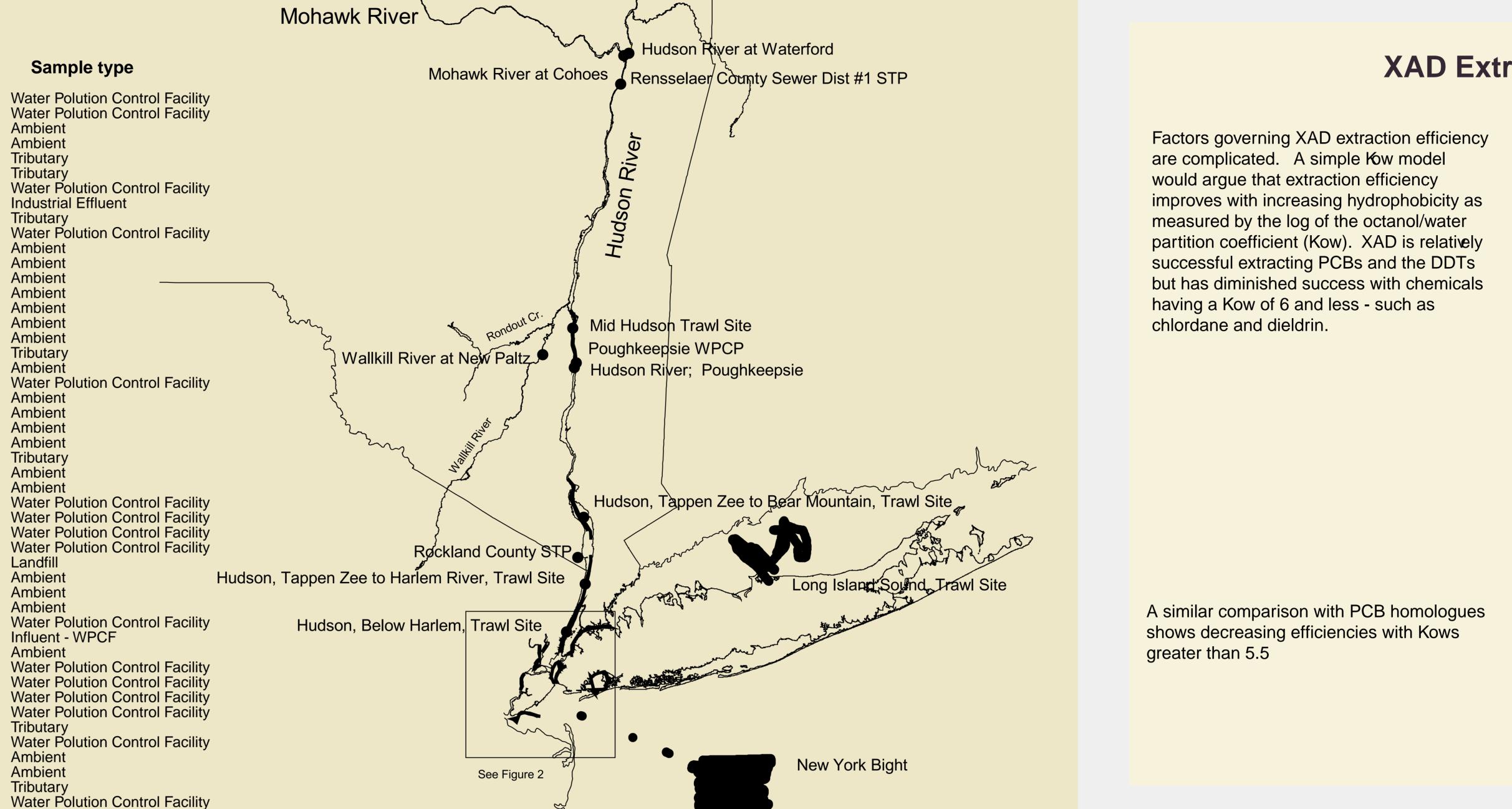
## **CARP Sample Sites** Sample type Gowanus Canal (Carroll St) Jamaica Bay, Trawl Site Water Polution Control Facility Water Polution Control Facility Oakwood Beach, WPCF Pelham Bay Landfill Holding Tank Passaic River, Mouth, Surface, Trawl Site Port Richmond, WPCF Red Hook WPCF

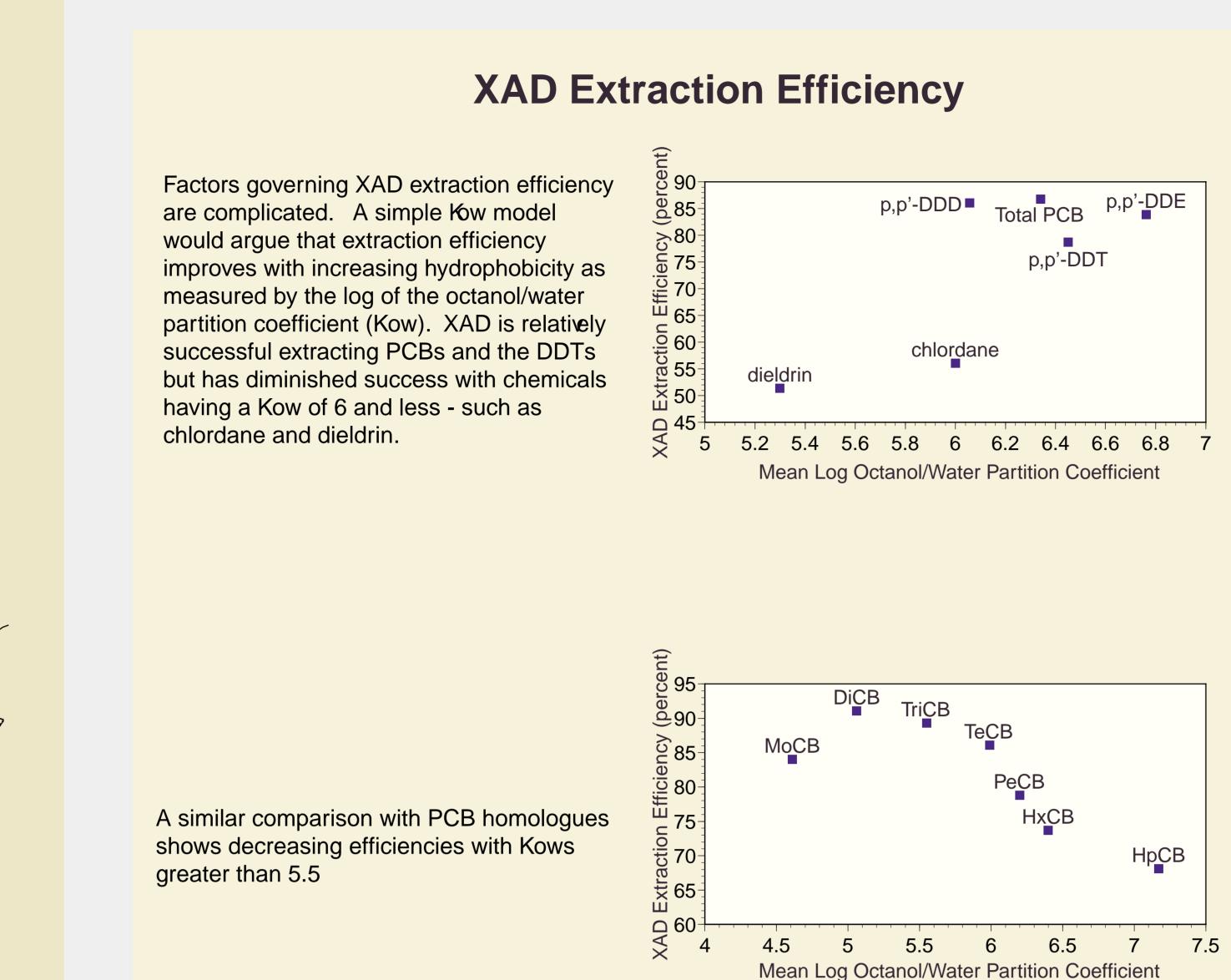
Saw Mill River, Yonkers

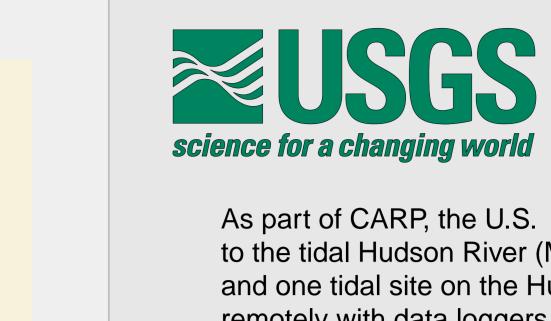
Tallman Island, WPCF

TOPS shipboard operation

Upper East River, Trawl Site Upper NY Harbor, trawl Site







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.

### **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).

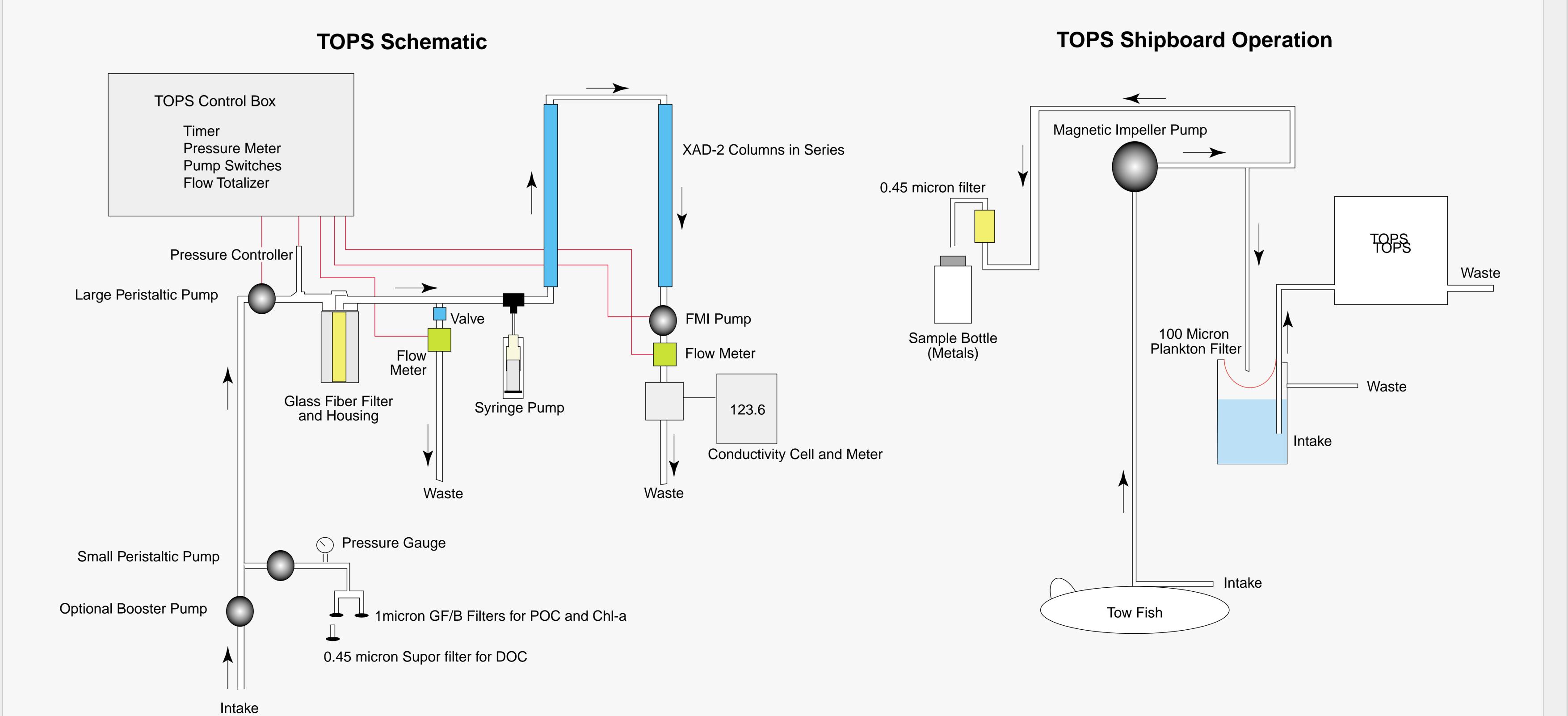
Once sampling is initiated the volume of water passing the stream gaging station is calculated by a data logger and calls are made to a data logger at the downstream sampling shelter each time X cubic feet of water pass the gaging station. An event usually entails several hundred calls between data loggers/shelters.

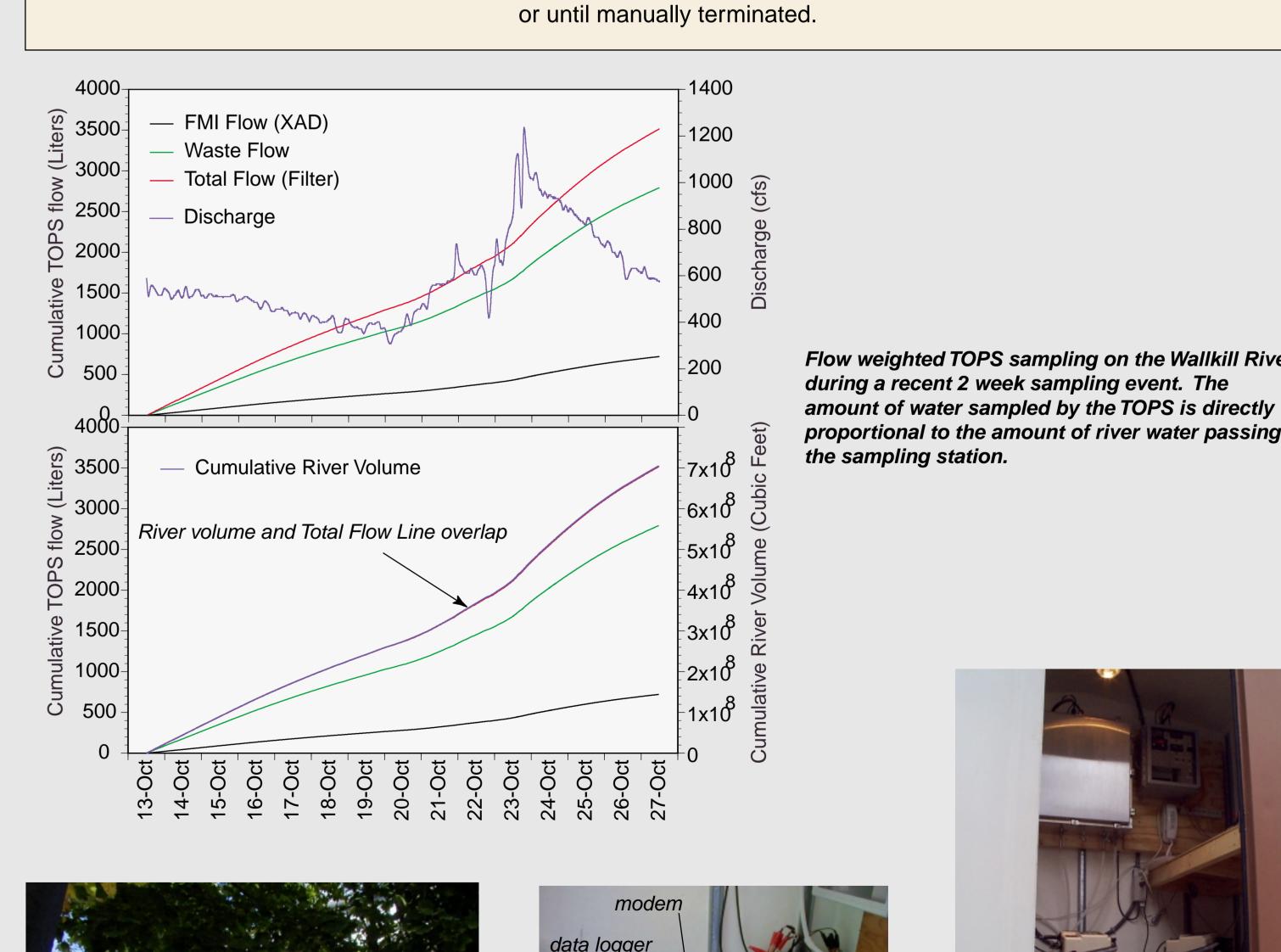
The sampling station data logger operates the TOPS based on the timing of calls from the stream gaging data logger The TOPS is run following each call until a fixed volume of water is pumped through both the filter and XAD.

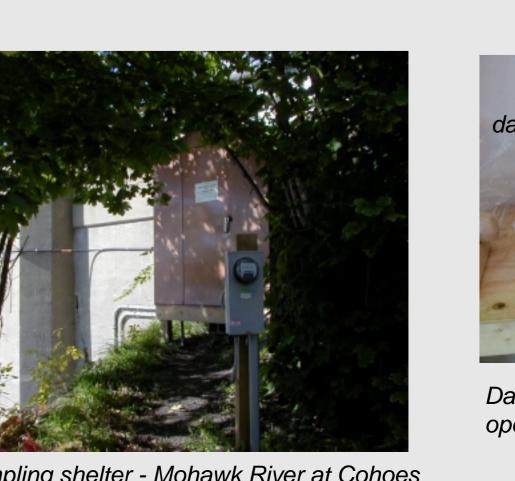
> Dissolved PAH samples are collected with one of the automatic pumping samplers as a sub-sample of the number of times the TOPS turns on and off.

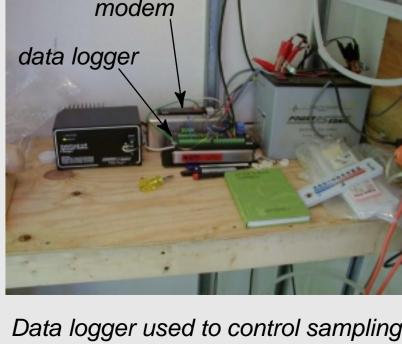
Sediment and TOC samples are collected over the storm hydrograph based on changes in stage and time between samples.

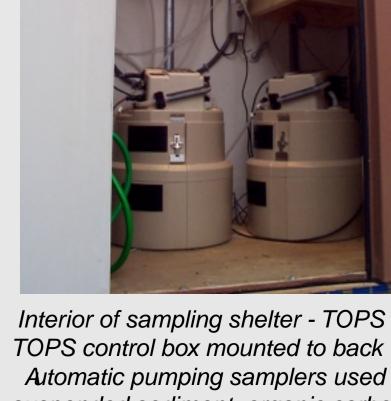
Sampling continues until the the stage falls to 80% of the difference between the event start and peak











dissolved PAHs are on floor

operations and communications USGS Sampling shelter - Mohawk River at Cohoes