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NY/PE DATE: 7/13/92

TO: Al DiBernardo

Enclosed are copies of pages with my comments +/or grammatical corrections

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T.R.E.S

BLOOMFIELD, N.J.

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NEW YORK STATE SOCIETY
OF PROFESSIONAL ENGINEERS

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current conditions in locations where low resolution coring is not performed. To the extent that they do not, then the estimates will not provide a direct indication of current sediment levels and additional low resolution coring may be required.

2.2.2.3 Other Data Collection Tasks

Two other data collection tasks are planned for Study Area B: sampling to assess scourability for contaminant transport modeling (Section 5) and sampling related to the ecological risk assessment (Section 7). These tasks are described in the referenced sections of this Work Plan and in the Phase 2 Sampling Plan (Appendix A).

2.2.3 Study Area C: RM 55 to Federal Dam

Study Area C represents the northern, freshwater portion of the Hudson River estuary. The downstream boundary at River Mile 55 was selected, because it is considered to be the average upstream limit of the salt front.

The main objective of the Phase 2 investigation in Study Area C is to evaluate the relative importance of loading from Study Area B to the overall PCB load in Study Area C. An estimate of Upper Hudson PCB loading to the estuary was provided in the Phase 1 Report. Additional data as previously discussed will be generated during Phase 2 to update that estimate. Available historic data poorly accounts for the contribution of the Mohawk River to overall PCB releases to the estuary; during Phase 2, both water-column samples and a high resolution core will be obtained within the Mohawk. Data obtained from these samples will be used to estimate current and historic PCB loads contributed by the Mohawk to the Upper Hudson and, in turn, to the estuary.

(No water column samples!

High resolution coring is the only sampling task scheduled for Study Area C. High resolution cores to be obtained at several locations within Study Area C will be analyzed for congener-specific PCBs and a range of other parameters, which are necessary to evaluate adequately contaminant fate and

and 2) the ecosystem and sediment geochemical characteristics upstream of the salt front are different from those below the salt front.

The focus of investigations in Study Area D will be to establish the significance of current PCB releases from the Upper Hudson (Study Area B) to the total contaminant burden found within Study Area D by determining the relative importance of various PCB inputs from the sediment records and other available release data to the estuary. Once an estimate of the relative burden contributed by various sources has been established, an assessment of the significance of remedial actions in Study Area B on Study Area D can be made.

A number of sediment cores will be collected within Study Area D for purposes of high resolution analysis (see Figure 2.7). These cores will be analyzed in the same manner as high resolution samples collected elsewhere in the Hudson and the resulting data will be evaluated similarly. Using the suspended load estimates derived from the high resolution core samples and literature data, total water column PCB concentrations will be computed for current and historic conditions. Since high resolution samples are to be analyzed for PCBs on a congener-specific basis, the historic PCB congener profile will also provide significant additional insight about sources of the contaminant load. Figure 2.8 shows the historic high resolution core locations for Study Area D.

Need samples to confirm [illegible]

The high resolution core program for Study Area D must be considered in the context of the total effort described in this plan. Data derived from sediment cores collected in all four study areas will be needed to evaluate PCB sources and loads within Study Area D. For example, trends in congener patterns observed in Study Area C samples should continue into samples collected in Study Area D. Therefore, shifts in congener patterns, for example, from an Aroclor 1242 pattern to one representative of a more heavily chlorinated Aroclor, are expected to be observable when all the high resolution core data are compared. The presence of a discernible congener pattern change from north to south may imply different sources.

3. MAIN DATA COLLECTION TASKS

This section presents a detailed discussion of the main data collection tasks, *i.e.*, congener analyses, water-column sampling, sediment sampling and geophysical surveys, in order to explain how the data derived from these tasks will be specifically utilized for analyses in Phase 2. (Section 2 provides an overview of these tasks for the general reader and summarizes data collection activities by study area.)

3.1 Congener-Specific Analysis of PCBs

As noted in the Phase 1 Report and elsewhere, the nature of PCB compounds is relatively complex. There are ten homolog groups, varying from one to ten in the number of chlorine atoms attached to the biphenyl molecule. Within each homolog group there exists a range of isomers, which vary based on the positioning of the chlorine atoms around the molecule. The number of isomers per homolog group varies from one for decachlorobiphenyl to forty-six for pentachlorobiphenyl. Collectively, the isomers are called congeners and refer to the 209 individual compounds classified as polychlorinated biphenyls.

The importance of this distinction in PCB classes arises from the means by which PCBs were produced and eventually released to the environment. PCBs were produced for industrial use as commercial mixtures called Aroclors, which typically contained several homolog groups, each containing many congeners. Analyses of PCBs in the environment have been reported historically on an Aroclor basis. This analytical approach became questionable, when it became generally known that Aroclor mixtures released to the environment did not remain there unaltered. Instead the mixtures undergo various processes, such as adsorption, volatilization, oxidation and degradation, which alter the present Aroclor mixture.

replace or original

either/or

In order to assess the impact of these processes, which vary in degree throughout the Hudson, PCB analyses will be necessary, first on a congener-specific basis. For example, in some cases the variation in congeners within a single homolog group may be used to define a specific geochemical process. Congener-specific analysis can also be used to differentiate newly released Aroclor mixtures from relatively older, altered congener mixtures.

Congener-specific analyses are proposed for all PCB analyses in Phase 2, because of their ability to differentiate fresh Aroclor mixtures from each other, to separate altered from unaltered mixtures and to differentiate the net effects of the various geochemical and biodegradation processes. Figure 3.1 illustrates the differences among several standard Aroclor mixtures on a homolog basis. Even with these limited 10 basic divisions, differences among the mixtures are clear. When congener analyses are applied to environmental samples, these distinct Aroclor signatures plus the alterations as a result of various processes become evident.

In this study, congener-specific analysis is defined to include the separation of the sample PCB mixtures by gas chromatography into a maximum of about 120 peaks (two to three congeners are occasionally represented by a one peak). Nevertheless, the level of separation to be achieved is sufficient for the necessary resolution of data.

3.2 Water-Column Sampling and Analysis

As part of the investigation in Phase 2, a set of water-column samples will be collected from the Upper Hudson (Study Areas A and B). These samples will be analyzed for a number of parameters and used to examine both current PCB loads and geochemical processes affecting those loads.

The data collection program for the water-column consists of four separate subtasks:

- Water Column Transects Sampling;
- Water Column PCB Equilibrium Study;
- Flow-Averaged Water Column Sampling; and
- Analysis of Historic Water Column Samples.

preservation of samples?

The dissolved and suspended matter phase PCB congener analyses are required to describe the flow-averaged total PCB concentration. The information will not be equivalent to the water column transect sampling, since the flow-averaged samples will be held for as many as several weeks before filtration, allowing the PCB distribution to equilibrate and losing the information on potential source type. Thus, the two sampling methods complement each other. The water column transect sampling gives instantaneous congener-related conditions, which can be used to locate contaminant sources and examine the effects of biogeochemical processes while generating an instantaneous PCB loading. The flow-averaged samples describe the mean total PCB loading, but potentially the congener distribution needed to identify specific sources and biogeochemical processes is altered.

The dissolved organic carbon and total suspended solids analyses will also be performed on a flow-weighted basis. These parameters are needed for the same reasons as for the water column transects.

The standard water quality parameters, pH, temperature, conductivity and dissolved oxygen, will be recorded at the time of sample collection. These data will be used qualitatively in support of the other parameters.

3.2.4 Analysis of Historic Samples

Scientists of the Lamont-Doherty Geological Observatory, between 1977 and 1986, have collected water-column samples for PCB analysis. These samples were separated into dissolved and suspended matter fractions, analyzed using packed column gas chromatography and archived. These samples are available for reanalysis on a congener-specific basis for the Phase 2 investigation and will provide information on the types of PCB congener mixtures historically carried by the Hudson River. The data will be compared with current congener mixtures to establish how the mixture has changed over time.

Geochemical application of these radionuclides is diverse and well-documented. They are utilized in lakes, rivers, oceans and estuaries as time markers or clocks for establishing sediment deposition rates. The power of the techniques arises, in part, from the simplicity of measurement. Radionuclides in sediments are analyzed by simply drying the sediment and placing it in a gamma spectrometer where the gamma radiation given off by the radionuclide can be measured and recorded. The sample is left in the counter for a period of hours to days in order to accumulate sufficient counting statistics. Once counted, the sample can then be used for other chemical analyses as needed. The sensitivity of the measurement is quite high. Typical detection limits are 200 picocurie per kilogram (pCi/kg) for Be-7 to 25 pCi/kg for Cs-137. (A picocurie is a measure of radioactivity. One picocurie represents ~~about 2~~ 2.2 disintegrations per minute.)

2.2 dp: Why say about?

Radionuclides in the sediments are used in two ways, as a clock in the case of Be-7 and as an event marker in the case of Cs-137. Be-7 is a naturally occurring radionuclide produced in the upper atmosphere by cosmic radiation. Its rate of fallout is fairly constant with time. The fallout rate at Albany has been measured at 0.018 pCi/cm^2 day (Olsen, *et al.* 1984).[2] Because its input is relatively constant with time, Be-7 is suitable for use as a sediment clock. For Be-7 the clock is started at the time of sediment deposition. Because Be-7 exhibits an exponential decay with a half life of 53.3 days, it will only be detectable in sediments for six months to a year, and virtually all of the Be-7 will be decayed after one year. Thus, the Be-7 clock is limited to the uppermost sediment layers, typically 2 to 4 cm in depth.

Cs-137, on the other hand, is an anthropogenic radionuclide, produced in atomic weapons testing and nuclear power reactors. Most of its release to the environment has resulted historically from atmospheric weapons testing. The historic input of Cs-137 to the New York area has been summarized by Bopp *et al.*

[2]Olsen, C.R., I.L. Larson, R.H. Brewster, N.H. Cutshall, R.F. Bopp and H.J. Simpson. 1984. "A Geochemical Assessment of Sedimentation and Contaminant Distribution in the Hudson-Raritan Estuary." NOAA Technical Report NOS OMS 2, U.S. Dept. of Commerce.

flood events. Potential scour must be assessed in detail, but not necessarily the exact details of flood transport.

5.1 Component 1 - PCB Mass Balance Analysis

The objective of this component is to predict the PCB levels in water and sediment on a year by year and reach by reach average basis. It will be used to analyze the potential impacts of various remedial and source control schemes, and will provide the input to Component 2, from which fish burden impacts will be estimated. We will organize the mass balance analysis using the EPA modeling package WASP4 (version 4.31, EPA CEAM, Sept. 1991).

5.1.1 General Concept and Level of Detail

The mass balance analysis can be implemented in two stages, of which the second will be a detailed application. The first stage involves completion and evaluation of a general inventory of PCB stores and fluxes, and associated uncertainties. This serves to provide the "reality check" on more detailed analyses. In the second stage, the mass balance approach will be extended into a large-scale, long-term, *quasi-steady* model of PCB behavior in the system.[2] This is generally the approach that Thomann *et al*. used for the Lower Hudson (although there are a ~~number of~~ several specific criticisms of their methods and assumptions.) Where our interest is in temporal and spatial average conditions, we can model long term PCB behavior by discretizing only to the spatial level of reaches with a seasonal time step for output, using WASP4. The transport portion of WASP4 is essentially a mass-balance accounting by segment. Thus, WASP4 provides the "accounting" framework in which to pose and answer questions relating to the mass balance.

The mass balance approach of WASP4 cannot handle the detailed simulation of a major flood/scour event and corresponding rapid redistribution

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[2] *quasi-steady* here means that sediment derived inputs change only gradually with time and catastrophic releases are not modeled.

5.1.5 Uncertainty Analysis

An important part of the mass balance will be the assessment of uncertainties. Confidence bounds will be developed for each significant store and flux in the mass balance. The cumulative impact of uncertainties will be assessed through implementing the mass balance model in a Monte Carlo simulation mode.

5.2 Component 2 - Biotic Effects/Fish Population Response

The previous section covers methods to estimate the long-term, steady-state environmental distribution of PCBs in the Hudson. This in itself does not yield decision criteria for the Reassessment: such criteria depend on analysis of risks, and human health risks are presented primarily through PCB levels in the fish population. Thus, the Reassessment requires us to estimate future concentrations in the fish population. PCBs may also present direct ecological risks to the fish population. To accomplish this we propose the use of a correlation analysis approach which relates observed fish PCB burden simultaneously to concentrations in both water and sediment.

Several ~~A number of~~ possible strategies were considered for the prediction of PCB ~~burdens in the~~ fish population, from the very complex to the very simple. A complex approach, which has previously been tried in the Lower Hudson[9], constructed a detailed model of PCBs in the food web, thereby enabling prediction of bioaccumulation. The other extreme is to assume a simple equilibrium partitioning approach, which attempts to relate the concentrations in target species to PCB levels in either the water or sediment, via a bioaccumulation factor (BAF). The approach proposed is related to the BAF approach, but does not require simplistic full equilibrium assumptions. This constitutes a multimedia correlation analysis, which can be thought of as a multivariate BAF which does not impose the assumption of equilibrium between the sediment and water

[9] Thomann, R.V., J.A. Mueller, R.P. Winfield and C.-R. Huang. 1989. "Mathematical Model of the Long-term Behavior of PCBs in the Hudson River Estuary." Report prepared for The Hudson River Foundation, June 1989. Grant Nos. 007/87A/030 and 011/88A/030.

Models are good for determining bioaccumulation of PCB in fish, but what we need is the harmful effects of PCB in fish and when it gets down below 1 µg/g they will lower the limit again! (originally 1 25 µg/g)

seems to be that the benthic pathway into the food chain is essentially ignored. Application of the model resulted in a prediction that by 1992 the median PCB concentration in three to six-year old striped bass would be below the FDA threshold of 2 µg/g (wet weight). Although 1992 data are not yet available, the most recent data suggest that this prediction is unlikely to come true.

5.2.2 Equilibrium BAF Approach

Analysis of the historical database in Phase 1 has provided support for the idea that PCB concentrations in the fish population, on a lipid-adjusted basis, can be reasonably predicted directly from environmental concentrations without explicit modeling of population dynamics. The empirical evidence is summarized in Figures B.4-25 (reproduced here as Figure 5.2) through B.4-29 of the Phase 1 Report, as well as earlier work of Brown *et al.*[10] These show a strong linear relationship between summer average PCB concentration in water and lipid-adjusted PCB burden in fish. This suggests that summer average (*i.e.*, nonscouring) water concentrations provide an excellent predictor of fish concentrations, via a BAF. The strong relationship observed is even more striking when it is realized that it is accomplished without the benefit of a congener-specific analysis. Presumably, congener data would strengthen the predictive ability.

Of course, statistical correlations do not themselves imply either causality or the ability to extrapolate to future conditions. It is also clear that much of the statistical strength of the observed correlations between water column and fish PCB concentrations is due to a few early observations, in which PCB concentrations in both water and fish were high, while more recent observations are clustered about a constrained subsection of the line. This does not mean that the observed correlation is invalid; rather, it reflects the fact that concentrations in both fish and water have been relatively stable since 1981. Further, we must expect a certain amount of "noise" in any correlation

[10]Brown, M.P., M.B. Werner, R.J. Sloan and K.W. Simpson. 1985. Polychlorinated biphenyls in the Hudson River, recent trends in the distribution of PCBs in water, sediment and fish. *Environmental Science and Technology* 19(8): 656-661.

based on gross estimates of total PCBs rather than individual congeners given any shift in congener pattern over time.

The observations presented in Phase 1 address only the correlation between PCB concentrations in water and fish PCB burden. However, sediment stores of PCBs may also provide an important pathway into biota. In Phase 1 we did not develop a correlation between fish PCB burden and PCB concentrations in sediment, because of a lack of an adequate database: The direct sediment measurements we had for Phase 1 are primarily at two points in time (1978 and 1984) and, except for limited data in 1978, confined to a location (the Thompson Island Pool) where a contemporaneous database for fish concentrations does not exist. Further, most of the sediment data lack measurements of organic carbon fraction (foc), which is essential to calculating the dissolved and/or bioavailable fraction of PCBs in the sediments.

PCB analysis of dateable, high resolution sediment cores affords an opportunity to combine the signals of water column and surface sediment concentrations. Unfortunately, most of the core data prior to 1978 do~~es~~ not coincide with NYSDEC standardized analysis of fish PCB burden. In addition, the location of extant high resolution cores does not match the NYSDEC fish sample collection points. Thus, during Phase 1, it was not possible to examine the value of PCB data from dateable cores as a predictor of fish concentrations. The high resolution coring program proposed for Phase 2 will remedy this situation.

not fish season

For a system in which sediment and water are in equilibrium there is also a strong theoretical basis for the BAF approach. This is based on the concepts of equilibrium partitioning and fugacity, which imply, for equilibrium conditions, that a BAF approach should be as effective a prediction tool as any identifiable food web model.[11]

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[11]Di Toro, D.M., C.S. Zarba, D.J. Hansen, W.J. Berry, R.C. Swartz, C.E. Cowan, S.P. Pavlou, H.E. Allen, N.A. Thomas and P.R. Paquin. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals using equilibrium partitioning. *Environmental Toxicology and Chemistry* 10(12): 1541-1583.

6. BASELINE HUMAN HEALTH RISK ASSESSMENT

The Phase 1 Report provided a preliminary baseline human health risk assessment and indicated that there was an unacceptable human health risk associated with eating fish from the Upper Hudson River. To perform a final baseline risk assessment in Phase 2, additional data will be utilized, *e.g.*, 1990 and 1991 fish data, sediment, water-column and air monitoring data collected in Phase 2, and relevant new information on PCB health risks, if any.

6.1 Study Area B

The preliminary human health risk assessment for the Upper Hudson was presented in the Phase 1 Report. Where updated site-specific information can be obtained, it will be incorporated into the final risk assessment. This information falls into two categories: exposure assessment and toxicity information, as described below.

6.1.1 Exposure Assessment

6.1.1.1 Fish Consumption

The Phase 1 preliminary human health risk assessment adopted the average recreational fish consumption value of 30 g/day that is recommended by the USEPA for the fish consumption pathway. The Phase 2 baseline assessment will evaluate whether there are adequate data to justify a different, site-specific or region-specific, *e.g.*, northeast, value for fish consumption that would apply in the Hudson River area in the absence of a fishing ban. Additionally, the Phase 2 human health risk baseline assessment will provide a discussion of the specific population that is targeted by the intake estimate, *e.g.*, whether it is appropriate to target recreational or subsistence anglers, both in the absence of a fishing ban.

for subsistence anglers: whether it be better to starve to death in a month or face possible cancer 40 yrs. from now

8. Feasibility Study Analyses

The Phase 1 Report presented general response actions and potential clean-up technologies and process options for PCB-contaminated sediments in Study Area B. Engineering analyses and treatability studies will be performed in Phase 2 for utilization in the Phase 3 Feasibility Study.

8.1 Sediment Volumes and Areas

During Phase 2 the areas and volume of sediments within Study Area B subject to possible remedial action will be identified. Geophysical survey and confirmatory sampling data from Phase 2 will be used to identify likely depositional areas within the various reaches of the river and will, in turn, enable computation of the contaminated sediment volume. Together with the historical and recent or planned PCB analyses of the sediments, identification of approximate areas of sediment subject to possible treatment, *i.e.* sediment with PCBs exceeding preliminary remedial action criteria, will be made. The volume of sediment requiring treatment will also be analyzed in terms of PCB Concentrations and current and future availability to the water column and biota. A map of potential remediation areas and sediment volumes will be prepared to aid in the evaluation of remedial alternatives.

8.2 Technology and Process Option Screening

During Phase 1, ~~a number of~~ several established and innovative technologies within several response action categories were identified. These and potentially other technologies will be examined for their implementability. Those technologies that are infeasible to implement will be eliminated from further evaluation.

The criterion for elimination of a particular technology or process option during Phase 2 will be technical feasibility. Technologies or process options will be determined to be technically infeasible based on study area-specific factors. Conditions, such as a sediment matrix being incompatible with

8.4 Treatability Study Literature Assessment

During Phase 1, numerous ~~a number of~~ technologies were evaluated to assess their suitability for remediating the Upper Hudson's contaminated sediments. Technologies considered during Phase 1 included those associated with response actions not requiring sediment removal as well as technologies that would be components of actions involving sediment removal and treatment. Part of the program to be accomplished during Phase 2 will be to evaluate experiences at other Superfund sites where contaminated sediments are either being remediated or are about to undergo remediation. In addition, considerable developmental activity has been occurring within the private sector and by federal agencies on systems and technologies that treat contaminated soils; these developments were reviewed during Phase 1 and that review will be updated during Phase 2. Finally, several comments were received on the Phase 1 Report related to treatment technologies and these also will be further evaluated.

Must inclu treatment if removal is chosen

8.4.1 In Situ Remediation

Technologies in this category include engineered approaches to stabilize or cap sediments so that sediment-bound contaminants are not scoured and released to the water-column. The geophysical program described earlier in this work plan will generate significant new data describing the distribution and physical characteristics of contaminated sediments. That information will provide the basis for further evaluation of *in situ* engineered solutions; no specific treatability studies are envisioned with regard to *in situ* remedial response actions, such as capping and/or stabilization of sediments.

Alternatively, *in situ* treatment of contaminants may be accomplished through bioremediation whereby natural biodegradation processes are enhanced by manipulation of environmental conditions conducive to microbial activity. Bioremediation was discussed in the Phase 1 Report and it was reported that, as of that time, no full scale *in situ* programs had been conducted using those techniques. It is expected that the General Electric Hudson River Research Study (HRRS) will provide the most relevant data on the viability of *in situ* treatment.

samples will be analyzed for grain size distribution and total organic carbon content. Additional activities are noted below.

- Sediment samples will be visually examined for sediment texture and stratification for calibration of both the side-scan sonar and the sub-bottom profiling survey data.

- Cores will be photographed to record visible sedimentological structures.

- Some cores will be X-rayed to detect *in situ* density variations before extrusion of the core.

- Core samples will be extruded in the field for visual and manual examination.

- Surficial sediments (0 to 2 inches) will be analyzed for grain size distribution and for total carbon/total nitrogen content and total inorganic carbon content. (Total organic carbon content is obtained as the difference between the total carbon and total inorganic carbon analyses.)

A.2.4 High Resolution Coring

This task will involve the collection of sediment cores from locations in Study Areas A, B, C and D (see Section 2 for definitions). These cores will be analyzed for radionuclides on a two to four cm layer basis in order to establish the year of deposition of a given sediment layer. These same layers will be analyzed for PCB concentration on a congener-specific basis as well as other parameters. A total of 23 core locati~~ons have~~ has been chosen.

The Phase 2A effort will begin with core collection from Study Areas C and D. This effort, as outlined below, contains the same number of core locations as given in the Phase 2A Sampling Plan, although one location has been dropped from Area C and one has been added to Area B.

1. Cores will be collected from eleven locations in Study Areas C and D. Their locations are shown in Figure A.2.2.

recent data, the stations at Stillwater and the lower remnant deposit pool have been dropped from the Phase 2A program. Additional samples will be obtained from the Hoosic and Mohawk Rivers just upstream of their confluences with the Upper Hudson and on the Champlain Canal just above Lock 7. These stations are additions to the Phase 2A Sampling Plan.

- A sample will be collected during each transect sampling round from an off-site location to serve as a sampling blank.

- At each station, data will be collected on water column conductivity, temperature, dissolved oxygen, and pH.

- Water will be collected at each station for PCB analysis (in a 20-liter aliquot), dissolved organic carbon analysis, total suspended matter analysis, total organic carbon analysis on suspended matter, and chlorophyll-a analysis. A small subset of samples will be analyzed for PCBs using one liter samples. The total organic carbon analysis on suspended matter represents an addition to the Phase 2A Sampling Plan.

- Each 20-liter sample collected for PCB analysis at each station will be separated by filtration into a dissolved fraction and a particulate fraction. The samples will be filtered in the field as soon as possible after collection but no more than four hours after collection. Each fraction will be analyzed on a congener-specific basis.

- Four separate sampling events along the transect will attempt to coincide with low flow (less than 8,000 cfs at Fort Edward) to typify current low flow PCB transport conditions.

- Three separate sampling events along the transect will attempt to coincide with higher flow events to examine current high flow PCB transport conditions. When possible, these events will coincide with sustained high flow for at least one to two days prior to sampling.

how to allot for lock openings?

- Samples will be collected from north to south (upstream to downstream) while monitoring the flow at the USGS hydrographic stations in the Upper Hudson so as to generally follow the same parcel of water through the Upper Hudson River.

- During one low flow and one high flow event, two 20-liter samples will be collected at each station along