Locator No: WQMS93-004
Contribution No: 93-004

An Isolation/Containment Strategy for Time-Integrated Trace Organic Sampling

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Introduction

In response to planned dredging activities at the three U.S. Superfund Sites along the St Lawrence River, Environmental Conservation Branch-Ontario Region initiated the development of an isolation/containment strategy to be used in conjunction with an automated *in-situ* water sampler for the measurement of waterborne PCB's.
This process involved the identification of technical problems, the development of procedures and protocols to effectively eliminate the risk and/or occurrence of contamination with regard to sampling and sample processing, and the development of equipment to be used in association with an existing automated sampling system.
The principal approach adopted was to develop a containment strategy ensuring that sampling materials were maintained in a clean state throughout the life cycle of the sampling process, and procedures that could be carried out easily and effectively in the field.

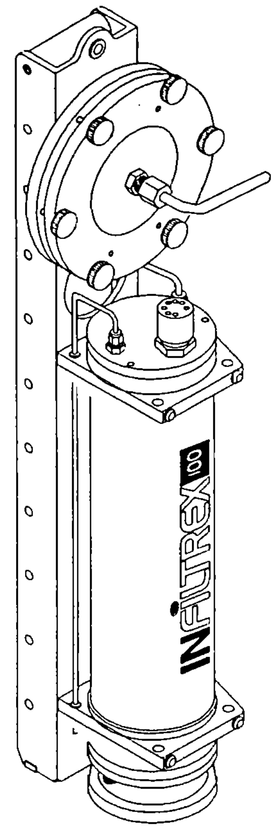
In terms of the technical aspects of this St Lawrence River water sampling program, the specific goals were as follows:

1) to collect time-integrated samples, isolated on glass fibre filters and XAD-2 resin, over consecutive 4-week sampling periods, for PCB congener analyses with a combined detection limit of 1 ng/L for total PCBs;
2) to maximize the representativeness of the time-integrated samples by minimizing gaps between the sampling events;
3) to develop simple and reliable field procedures;
4) to minimize sample blanks as well as variability between replicates; and
5) to maximize the overall data quality in order to achieve consistency in the data quality both within and between the time-integrated sample periods.

This report will provide, in Part-A, a description and assessment of the isolation/containment strategy employed in conjunction with the *Infiltrex* automated water sampler. A discussion of operational considerations for reliable automated sampling as well as an assessment of the *Infiltrex* sampler, which was deployed under a rigorous riverine setting, is provided in Part-B.

About the Infiltrex Sampler

The *Infiltrex* is an automated *in-situ* water sampler, which consists of a pump, a flow meter, a microprocessor and a power supply . It is usually equipped with a filter and a resin column for the concentration of contaminants from the particulate and non-particulate phases of large volume water samples. The operator programs the unit in the field with a portable computer by defining the following :



1) year, month, day, & time
2) station name
3) column identifier
4) flow rate
5) volume sampled per cycle
6) number of sampling cycles
7) interval between cycles
8) mode of start-up & start time

Sample control specifications are confirmed by the instrument prior to activation.

When activated, the sample flow rate is controlled by the microprocessor by monitoring the measured flow rate and adjusting the voltage supplied to the pump in order to achieve and maintain the desired sampling rate. The specified sample volume per cycle is the target parameter and, as such, the requested sample volume is typically processed, as determined by the flow integrator system. For each litre sampled, 36,000 pulses are generated by the flow meter. At programmed sampling rates of 100ml/min, the requested flow is quickly acheived and maintained owing to a corresponding high pulse rate of 60 pulses/second.

As sampling progresses, the filter system would normally become impacted with sediment. The voltage supplied to the *Infiltrex* pump would automatically increase in order to maintain the desired sample rate. If the specified sample rate can no longer be achieved the *Infiltrex* will, nonetheless, continue to pump sample water down to a 30mL/min cut-off flow rate, while extending the pumping period in order to deliver the target sample volume.

At the end of a programmed sample run, the *Infiltrex* will display through a computer link the start and finish times as well as the total sample volume in litres. Should sampling be terminated prior to the scheduled completion of a run, one of the following error messages will appear on the *Infiltrex* report:

a) shut down due to low flow
b) shut down due to power interruption
c) shut down due to low voltage

Part A - Development of an Isolation/Containment Sampling Strategy

A key component of the isolation/containment strategy was the preparation of modular, exchangeable assemblies (Fig. 1), which maintain the sampling materials in a clean state throughout the life cycle of the sample collection process. This isolation/ containment strategy is based on, and consistent with an approach developed for trace metal sampling in Pukaskwa National Park. Results of the ISOMET stream sampler program (McCrea, 1994) was presented at a previous workshop organized by the Coordinating Committee of the Canada - British Columbia water Quality Monitoring Agreement, held in 1993.

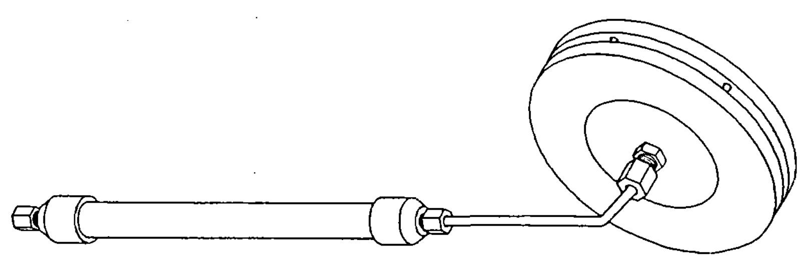


Fig 1. An illustration of a sealed Filter-Plate/Resin-Column modular assembly.

The use of freshly charged, verified, sealed, exchangeable assemblies, which are prepared under clean laboratory conditions, essentially eliminate sample handling in the field. As a result, contact of the filter and resin sampling materials is effectively and appropriately restricted to the water being sampled. The exchangeable assemblies also facilitate sample recovery under clean conditions upon return to the laboratory. An outline of the isolation/containment strategy, related QA/QC considerations for both field and laboratory elements is presented below.

An Outline of a Isolation/Containment Method for Trace Organic Sampling with the Infiltrex Sampler

A)- Filters and Resin Preparation

Glass fibre (GF) filters, which are inexpensive, easily cleaned, and readily extracted for sample recovery, were selected as the filter media of choice for our sampling program. The glass fibre filters (Sartorius; SM 134-142K) are solvent rinsed with acetone in a stainless steel filter apparatus at low pressure, heated at 50°C for one hour and overnight at 300°C. Filter blanks are obtained through standard gas-chromatographic analyses. Fresh XAD-2 resin is subjected to extensive cleaning, on a batch basis, using several solvents (acetone, hexane, & dichloromethane) with typical extraction periods of at least 15 days. Once shown to be appropriately cleaned for our sampling program, the resin is stored in methanol in sealed containers.

<u>QA/QC element</u> - Sample materials (filter & resin) are prepared under clean laboratory conditions and verified prior to use in the field program; these materials are prepared in batches for consistency purposes.

B) Filter-Plate/Resin-Column Assembly Preparation

For ease of assembly and deployment in the field, the length and bore of the tubing, as well as the fittings sizes were standardized. For quality assurance reasons, the filter plates, resin columns, and tubing are made of Teflon or stainless steel. For strength and reliability, stainless-steel Swagelock fittings were used, exclusively.

The assembly components are routinely soaked, for several days with a laboratory grade detergent, until all visible contamination (particules and pigments) are easily removed without the use excessive physical and/or abrasive cleaning strategies. After soaking, the components are then rinsed with copious amounts of distilled water, flushed with acetone, and sealed to maintain their integrity. Fittings are stored in pre-cleaned Teflon jars.

The week prior to a given re-deployment survey, the columns are packed with cleaned and verified resin and, the modular assemblies are then prepared under laboratory conditions. At both the intake of the filter plate and outlet of the column, Swagelock fittings equipped with threaded plugs are used to effectively seal the assemblies. Similarly, the intake tube is equipped with a Swagelock fitting/threaded plug at one end and a custom-built Teflon cap at the other which, combined, effectively seal the unit (Fig. 2). Immediately after the assemblies and intake tube have been prepared, they are secured in a custom-built assembly holder, which is mounted in a cooler. Both the assembly holder and cooler are thoroughly cleaned prior to use, and maintain the external surfaces of the assemblies in a clean state. In addition, they provide appropriate physical and thermal protection to the assemblies in transit as well as in the field.
QA/QC element- All components are prepared and assembled under clean laboratory conditions; the modular assemblies, which are physically and thermally protected, maintain the sampling elements in a clean state throughout the sampling process.

C- Deployment and Recovery of the Assemblies
At the field site, the *Infiltrex* samplers are attached to a buoy with two 0.25" stainless steel cables. One cable is "permanently" attached to the buoy throughout the entire field season. A second cable, of slightly longer length, is used to retrieve the sampler. The total re-deployment time, including flushing and re-calibration of the pump/flow meter system and the installation of replacement batteries is about 30 minutes.

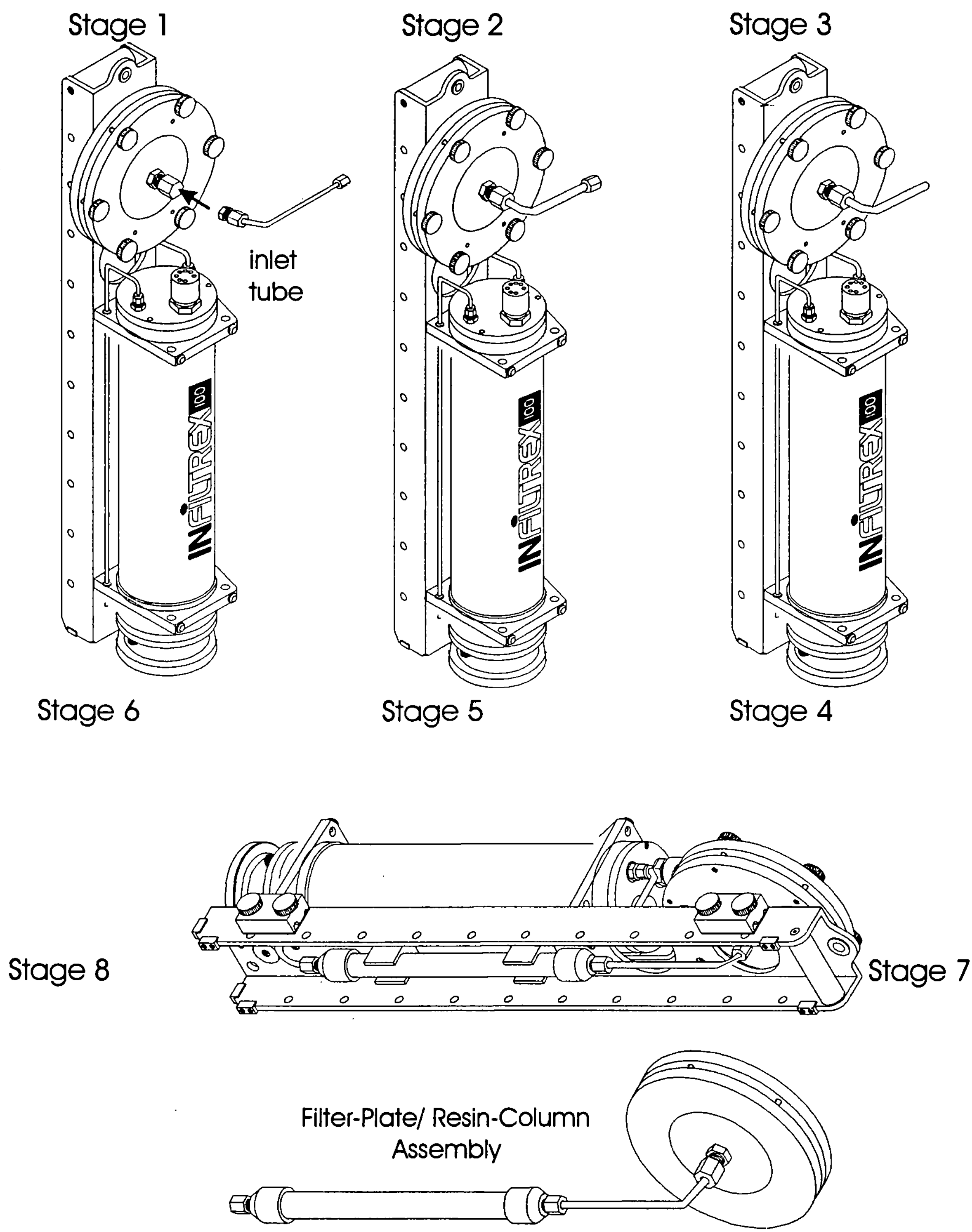


Figure 2. Deployment of an Infiltrex sampler using an isolation/containment strategy.

An Outline of Field Activities in the Deployment of the Infiltrex Sampler.

Infiltrex Deployment

Stage 1 With the assembly in a sealed state, mounted to the *Infiltrex sampler,* the flow metering system is verified and the instrument is programmed for the 4-week time-integrated sampling period.

Stage 2 The assembly is then connected to the *Infiltrex* pump line and the intake tube is attached to the filter plate inlet. The sampler is then mounted onto the mooring cable for deployment.

Stage 3 The sampler is lowered to the water surface; the inlet tube cap is removed immediately prior to submersion.

Infiltrex Recovery

Stage 4 After completion of the 4-week sampling period, the retrieving cable is dis-engaged from the buoy and the *Infiltrex* sampler is retrieved.

Stage 5 A clean cap is immediately placed over the end of the inlet tube to mitigate contamination.

Stage 6 After weeds entangled around the filter plate are removed, the intake tube is dis-engaged and a clean Swagelock plug is immediately threaded onto the filter.

Stage 7 With the *Infiltrex* placed in an horizontal position, the pump is initiated to draw the remaining water from the filter plate. At the first sighting of air in the tubing located at filter plate outlet, the pump is immediately shut off to maintain the resin column in a wet state. The plug on the filter plate is then tightened to seal the inlet. The fitting at the outlet of the column in then dis-engaged from the *Infiltrex* pump line, and immediately sealed with a clean threaded plug. The assembly is removed from the *Infiltrex* sampler frame and then secured in a cooler. Exposure of the sampling elements to the field environment is insignificant.

Instrument servicing and Maintenance

Stage 8 After data is down loaded from the *Infiltrex*, the pump and flow metering system is flushed with a water-methanol solution. Batteries are then replaced and a "new" assembly is bolted to the sampler frame. The instrument is then ready for re-deployment (see; stage 1).

QA/QC element- The use of exchangeable (filter and resin) assemblies effectively eliminate sample handling and processing in the field and, therefore, both systematic and random field errors common to many field programs are avoided.

D- Sample Processing

Upon return to the laboratory, the assemblies are dis-assembled under clean laboratory conditions. The GF filters are carefully removed from the filter holders, and immediately placed in solvent-washed Teflon jars. Both filter and the resin column are then submitted to the Wastewater Technology Centre (WTC) laboratory for analyses. The WTC method for PCB congener analysis is based on the U.S. Environmental Protection Agency's Standard Methods for XAD-2 resin and sediments. The particulate and dissolved fractions are extracted separately in Soxhlet-extractors for 12 hours (60 cycles in acetone/hexane). Once combined, the whole-water extract is concentrated and subjected to Snyder and florisil clean-up, before injection on a gas chromatograph. In total, some 30 injections including standards, method spikes, and arochlor references are performed with each batch of 5 samples. A summary of the analyses including those performed in association with the sampling material preparation, is presented below.

1) Sampling material verification
    - filter blanks
    - resin blanks
2) Analytical process verification
    - method blank
    - method spike
    - internal sample surrogates: PCB-30, PCB-65, OCN
3) Analytical standard / reference
    - arochlor reference 1016, 1232, 1242, &1254,
    - total PCB standard 2 : 2 : 1
      1242 / 1254 / 1260

In order to achieve the reliable quantification of the PCB-congeners of interest in the St Lawrence River, a target 200-litre sample size was established in consultation with the WTC laboratory to obtain a combined 1 ng/L reporting limit for total PCB.

Results

Correspondence of Replicates and Overall Data Quality

As part of the sampling program, a second sampler was installed at the station located along the south shore of the St Lawrence River, for replicate analyses purposes. The intake tubes of the replicate samplers were within 0.5 metre of each other. A summary of the replicates results is presented below.

Replicate Data Collected at Stn-2 (total PCBs ng/L)

$Stn\text{-}2_{R1}$	$Stn\text{-}2_{R2}$	Difference
1.5	1.7	0.2
2.1	2.1	0.0
1.0	1.1	0.1
1.7	2.1	0.4
1.2	1.4	0.2

$\bar{x}$ $Stn\text{-}2_{(R1+R2)} = 1.6$

Range in difference between replicates	0 - 0.4 ng/L
Median difference between replicates	0.2 ng/L
Median resin blank	0.2 ng/L
Median method blank	0.2 ng/L
Analytical reporting limit for total PCBs	1.0 ng/L

The correspondence between replicates, which are a measure of total variability including all field and laboratory aspects, was excellent. If we calculate the mean values for Stn2, then the difference between the replicates and their respective mean, would be half that shown or typically 0.1 ng/L. Although, the total PCB concentrations were near the analytical reporting limit, on average, the difference between replicates and their respective mean was only 6%. It is interesting to note that both the median resin and method blanks were of equal magnitude to the median difference between replicates.

In summary, the use of freshly charged, verified, exchangeable assemblies, effectively eliminated contamination in the field and, therefore, provided time-integrated samples of high, consistent and definable quality.

Part B - Operational Considerations for Reliable Automated Sampling

In order to ensure reliable deployment of an automated water sampling systems, the instrument must have an appropriate:

1) event sampling configuration;
2) filter system;
3) flow meter and flow integration system; and,
4) power source.

Prior to the commencement of this sampling program, a review was undertaken to assess the key elements. Modifications to the operation of the *Infiltrex* sampler were then made to meet our specific requirements, which are discussed herein. In addition, operational considerations relating to the use of the modular assemblies are also presented.

Operational Advantages of Modular Assemblies

The use of verified, exchangeable assemblies allowed for the collection of high quality samples. In addition, it greatly reduced sample handling and processing in the field and, as a result, the re-deployment of the *Infiltrex* samplers could be carried out at the buoy site in about 30 minutes, from a small craft. Otherwise the samplers would have had to be taken to a site on shore where the assemblies could be dismantled and the sampling materials recovered. In field programs, where sampling is conducted distant from a laboratory, a field station equipped with cleaning facilities and a fume hood would have been required to appropriately clean the filter plates and tubing, as well as to recover the samples. In terms of cost, the time required to carry-out each survey would have been at least one or possibly two days longer, adding between 10 and 15 person days to the sampling program. In addition, the cost of establishing an appropriately equipped field station, where required, would have been much greater.

Another advantage of using modular assemblies is that the instruments can be re-deployed within one hour of the previous sample recovery. Using traditional sampling strategies requiring servicing onshore, there would have been a 1 to 2 day gap between sampling periods.

QA element Modular assemblies can significantly reduce the time between re-deployments and, therefore, can improve the temporal representativeness with consecutive time-integrated deployments. Modular assemblies are also cost effective.

Event Sampling Configuration - Representativeness of Time-Integrated Samples

The approach adopted in our study was to maximize the number of sampling events within a run, in order to minimize the temporal uncertainty. With the adoption of a 4-week integrated sampling period, the number, volume, and scheduling of the individual events within the integrated run was reviewed. The number of programmable events available with an *Infiltrex* sampler is normally 99 events per run. Distributed over a four week period, this would allow for a maximum sampling frequency of one event every eight hours. Following discussions with the instrument manufacturer staff (AXYS, Sidney, B.C), re-writing of the software was undertaken to allow for the collection of 255 events per run. As a result, sample collection at 3-hour intervals, with each sampler, was then possible over the entire 4-week sampling period. Combined with a 1-hour staggered start-up time between the three samplers, moored along a transect downstream of the dredging site, allowed for sample collection each hour of every day throughout the entire sampling program. In total, 220 events could be sampled at each site. Given the 200L target sample size for PCB analysis, a sample volume of 1-litre per event was adopted and, subsequently, a sample flow rate of 100 ml/min was selected, yielding 10-minute integrated sampling period per event.

QA/QC element- The increased number of sampling events available per run, combined with staggered deployments, reduced the gap between the pumping events and, therefore, improved the overall temporal representativeness of the sampling program.

Filter Considerations

Numerous filter systems are available from AXYS as well as other suppliers, which could be used for the removal of suspended solids. Metal cartridge filters, which can provide effective filtration for waters containing elevated sediment, were discounted owing to concerns relating to sample extraction and cleaning for subsequent re-use. In terms of filter preparation, glass fibre filters were considered to be most appropriate for solvent extraction and thermal treatment for the removal and destruction of trace organic contaminants. Glass fibre filters, which are easily cleaned and relatively inexpensive, were thus selected as the filter of choice for this sampling program. Of the various filters available, the extra thick Sartorius GF filters (SM13430-142K) were chosen for both their strength and additional filtering capacity. With a thickness of 1.55 mm, the SM13430 filters are approximately three times thicker than standard GF filters.

QA element The glass fibre filters are easily cleaned and have extremely low blanks.

For ease of sediment recovery, the *Infiltrex* pump is activated for some 10 seconds shortly after the sampler has been retrieved in order to remove all water from the filter plates while maintaining the XAD-2 resin column in a wet state. Upon return to the laboratory, the filter plates are dis-assembled. The near-dry GF filter is then folded several times and then immediately placed in a solvent washed Teflon jar for later extraction in a Soxhlet system.

Over the course of the study, the Sartorius GF filters provided effective filtration, as not a single sample run was prematurely terminated due to filter clogging. In fact, it appeared that the filtering system may have been capable of filtering perhaps 500 or even a 1,000 litres of St Lawrence River water. Aside from the enhanced capacity of the high sediment load Sartorius (13430) filters, the effectiveness of the filtering process was largely attributed to the orientation of the filter plate in combination with sampling regime.

In our sampling program, the average velocity across the filter was about 5 mm/min. Given that the *Infiltrex* samplers were programmed for 1-litre events with on/off time schedule of 10 min [on] and 3 Hrs [off], only small volumes of river water were drawn through the filters, at any one time. Under these conditions, much of the suspended sediment attenuated by filter, did not become entrained into the "pores" of the filter. Instead, it largely accumulated along the lower edge of the filter plates forming a wedge of sediment. Even by the end of the sampling run (220L) the top 3/4 of the filter remained relatively unclogged, and capable of processing much larger volumes of river water then was required for this program.
QA element Automated time-integrated sampling, with numerous small volume sampling events would appear to greatly facilitate the processing of large volume samples with the filter plate in a diagonal to vertical orientation.

Flow Meter System
The *Infiltrex* is equipped with a Type-1 IR-Opflow Precision flow meter. It is intended for use in pumping applications ranging from 100-2,000 ml/min, and generates 36,000 pulses per litre. At our target flow rate of 100 ml/min, the flow meter yields 60 pulses/second and, as a result, the target flow rate is achieved quickly and reliably by the *Infiltrex* sampler. Verification of the flow metering system prior to and at the end of each sampling run has demonstrated an impressive level of consistency.
QA element - The *Infiltrex* flow meter and flow integration system was accurate, and consistent.

In our 1995 sampling program, we had three *Infiltrex* samplers suspended from Gillman buoys and four samplers from navigational buoys located in the shipping channel. All samplers were deployed in reaches with relatively high current (3-7 knots) resulting in severe wire angles. At our Gillman buoy sites, flow meter failures were minimal. A few failures were, however, observed on samplers suspended from the navigational buoys. Flow meter failure, at the latter sites, was attributed to turbulence caused by the ocean going vessels, which would often pass within 20 metres of these buoys. AXYS staff have indicated that flow meter failure is relatively uncommon in other applications. The IR-Opflow meter is rigidly secured within the *Infiltrex* sampler housing, and vibrations on the buoy and mooring cable are likely to be transmitted to the body of the flow meter. Given that the IR-Opflow meter is not designed for use in applications with severe mechanical vibration, it is our intention to couple the flow meter with soft silicon tubing from the pump to exit port to effectively dampen vibration and eliminate sampler failure in our future deployments. It should be recognized that our St Lawrence River sampling is conducted at a depth of 5 metres. The use of soft tubing at greater depths would not be appropriate.

Power Supply Considerations for Infiltrex Sampler

The *Infiltrex sampler* is powered by two 6-volt (lantern) batteries aligned in series; a large capacitor provides a two-hour memory back-up. An external battery pack is also available from AXYS Environmental Systems, which will significantly increase the pumping capacity of the *Infiltrex* sampler.

Field testing of the *Infiltrex* sampler, in March 1995, demonstrated that there was insufficient energy in standard alkaline lantern batteries, that we tested, to pump the required sample size (200-litre) for our program, during cold water conditions. Comparison of batteries from the major manufacturers is difficult since they do not normally provide energy specification, and it has been our experience that the amp/hour output may change without notice.

QA element Battery load tests should be performed by users of *in-situ* automated water sampling equipment to ensure reliable sampling.

Upon closer examination, it was ascertained that lantern batteries are made up from stacked 1.5-volt cells, which are press fit and sheathed with a metal wrapping. As a result, there are numerous un-secured contact points within each battery. Momentary failure of a single contact or battery would terminate a sampling run.

Given the high river current and turbulence in this reach of the St Lawrence River, there was a concern for the security of the power supply. Since there was a need for both more and secure power, an auxiliary power supply was developed.

Our custom-made auxiliary power supply was fitted with 12-volt cells fabricated from eight "C" cells, which were welded together with nickel strapping, and sealed with heat shrink wrapping. The welded cells were manufactured by the Battery Company (Buffalo, New York), at a cost of $11 US per unit. Over the course of our sampling program, the welded cells provided a secure source of power and, as expected, there was not a single power failure in over 60 deployments.

QA element- Hard-wired welded cells have proven to be extremely reliable even in rigorous stream applications, such as those found in the shipping channel of the St Lawrence River.

In future applications, it is our intention to remove the lantern battery housing from within the *Infiltrex* sampler and mount the welded battery packs directly into the instrument. The *Infiltrex sampler* can accommodate up to four sets of 12-volt welded cells. This set-up would provide an appropriate and secure power supply for our application, and would be capable of reliably pumping over 300 litres in cold water applications, and up 700 litres in warmer water. It would also greatly reduce the severe drag that we have experienced in this high velocity reach of the St Lawrence River. The cost of the 12-volt welded cells are insignificant in terms of the program costs and would effectively eliminate the need of acquiring an auxiliary battery pack. The Battery Company are currently developing welded-cell rechargeable alkaline battery packs, which are not expected to suffer from the memory problems common with nickel/cadmium systems.

QA element Replacement of the battery housing in *in-situ* instruments with welded cells can greatly increase the pumping capacity and reliability of automated water sampling system.

Summary of Results and Conclusion

1) The *Infiltrex flow* metering system was consistent, accurate, and appropriate for low level contaminant work.

2) Hard wired welded-cells provided a reliable source of power; not a single sample was lost due to power interruption or power shortage. This power supply configuration should be considered for use *in-situ* instruments deployed under rugged conditions.

3) Glass fibre filters provided effective filtration; not a single run was terminated due to filter clogging. Sediment was readily extracted from the filters, and filter blanks were insignificant.

4) Reprogramming the *Infiltrex* microprocessor for an increased number of sampling events was effective, and it enhanced the temporal representativeness of the time-integrated samples.

5) The integrity of the water sampling program was very good as all "total" method blanks were well below the analytical reporting limit.

6) The development of an isolation/containment strategy for use with the *Infiltrex* automated sampling system was effective. It minimized gaps between the integrated sampling periods, significantly reduced field work and related field costs and, more importantly, provided data of high, consistent and definable quality.

In conclusion, much of the complexity of sample handling and processing commonly undertaken in the environmental quality field programs should be avoided, where possible. This is particularly important for studies of trace contaminants where the risk of sample contamination is high. The use of modular assemblies greatly simplifies the sampling process, and mitigates the potential for contamination and, as a result, data quality objectives can be readily and reliably achieved.

Acknowledgments

I would like to thank Jim Bull, Klavs Davis, Neils Madsen, Harry Savile, Erwin Smith, and Al Tyler of NWRI engineering for the design and fabrication of equipment related to this project; Ken Hill, John Kraft, Mike Mawhinney, Barry Moore, Ross Neureuther, Steve Smith, and Earl Walker of NWRI, technical operations, for their efforts in deploying and retrieving the sampling equipment; Bob Gay and AL Read of Fisheries & Oceans Canada for deploying the buoys. Special thanks are extended to Mike Mawhinney for the mooring set-up and his support and consideration. I would also like to thank Tony Ethier, Stacey Jarvin, and Al Todd for their advice, and the willingness of AXYS staff to make modifications to their programming with little notice; Mike Comba, Klaus Kaiser, Gary Leppard, Jim Maguire and Bill Strachan of NWRI for their advice and assistance; Robert Hong-You and Lewina Svoboda of the WTC laboratory for their prompt and high quality analyses; Joe Kania for modifying and fabricating components; and to Mary-Lou Archer, John Fischer, Melanie Neilson, Don Williams, and Francis Philbert of the Environmental Conservation Branch for their contribution to this program. Special thanks are extended to Scott Painter for his support throughout the study, and reviewing this manuscript.