

**Standard Operating Procedure for
Site Selection and Sampling
for Mercury in Lakewater**

**Robert P. Mason and Kristin A. Sullivan
Chesapeake Biological Laboratory
University of Maryland
P.O. Box 38
Solomons, MD 20688**

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The mercury samples will be collected at all the master stations, as designated within the LMMB/MB plan (Figure 1). Samples will be collected from mid-depth at each station if the water column is unstratified, or from two or three depths during stratification. If a nephloid layer exists at the lake bottom, this will also be sampled. Water will be collected using Teflon-lined Go-Flo bottles that have been rigorously cleaned. All stages of field apparatus cleaning and preparation will be performed within a clean lab following strict trace metal protocols (Patterson and Settle, 1976), as adapted for mercury analysis by Gill and Fitzgerald (1985). This paper, which forms the basis of current sampling procedures and sample collection, is attached as Appendix 1.

Cleaning consists of an initial soaking in detergent, a MilliQ water rinsing and a further soak in dilute (0.05% HCl). A detailed outline of the cleaning and bottle preparation techniques is contained in Appendix 1. The Go-Flo bottles will be filled with laboratory grade MilliQ water and allowed to sit for six hours (i.e. significantly longer than the expected residence time of the sample in the bottle in the field) before sampling to assess contamination due to leaching of mercury from the Go-Flo bottle walls. Bottles showing any contamination will be recleaned. Initially, two Go-Flo bottles supplied by EPA will be used until additional Go-Flo bottles can be purchased, cleaned and checked. At least three bottles are desirable for periods when three depths are to be sampled per station. Additional bottles are also required as backups in case of loss or contamination.

After cleaning, and between deployment, Go-Flo bottles are stored in two or more polyethylene bags within a tight plastic or wooden container. Prior to storage, bottles will be rinsed with dilute acid and then MilliQ water. If contamination is noted or suspected, bottles will be returned to the UMCBL for cleaning. If the bottles are not to be used within 30 to 60 days, bottles will be shipped back to the UMCBL for rechecking of blanks and for cleaning and maintenance.

Details of sample collection procedures are also contained in Appendix 1. Sample collection will only be performed by personnel trained by UMCBL or another recognized laboratory in the methods of the so-called "clean techniques." Improper use of the Go-Flo bottles can result in permanent contamination. Handling procedures are detailed in Appendix 1. The PI, or a designated substitute, will be on site during each deployment and will be in charge of the planning and co-ordination of on-site activities. The PI will determine when to collect the mercury samples, after consultation with the ship's officers and other PI's on board. The PI will monitor the sample collection and determine whether the samples have been collected "without obvious contamination." If the PI feels that the sample has been compromised, a redeployment with one of the other Go-Flo bottles will be the designated contingency.

Go-Flo bottles will be deployed from non-contaminating Kevlar line. Bottle messengers will be Teflon-coated and the line weight will be non-metallic and Teflon-coated, if possible. Due to the nature of the activity i.e. the attachment of the bottles requires the personnel to reach out over the guard rail, the personnel should be attached to a safety line. Also, personnel should wear a hard hat and steel cap boots to prevent injury. Go-Flo bottles will be removed from the polyethylene bags as close to deployment as feasible and will be returned to the polyethylene bags as soon as possible after retrieval. Bottles will be transported around the ship within bags and water will only be decanted within the clean room on board ship.



Figure 1. Map of Lake Michigan Mass Budget/Mass Balance Study

Inside the clean room, water will be decanted, as soon as possible, from the Go-Flo bottles into acid-cleaned Teflon bottles. Two liters of sample will be collected for total mercury analysis (and for methyl mercury analysis even though methyl mercury measurement is not part of the LMMB). Laboratory replicates will consist of subsamples of water taken from the same Go-Flo bottle or from the same Teflon sample bottle. Field replicates will consist of duplicate deployments at the same sampling location. To ascertain the field blank, MilliQ water of known concentration will be added to an empty Go-Flo and allowed to sit for a period comparable to the deployment time before being decanted from the bottle. This blank will represent, as near as possible, the blank associated with all sources of contamination from field collection to analysis. All samples will be collected in acid-cleaned Teflon bottles. Trace metal grade acids will be used in all cleaning and storage stages. Potential for contamination will be minimized by prepackaging sample bottles in double polyethylene bags. Bottles, and acidification acid will be analyzed for contamination before use.

Particulate samples will be collected onto quartz fiber filters, of nominally $0.8 \mu\text{m}$ pore size. Filters will be cleaned of mercury by heating in a muffle furnace for 12 hours at 600°C . After cooling in situ, filters will be removed and stored in a bagged acid-washed Teflon vial. Filters will be placed, under clean room conditions, within an in-line Teflon filter holder. Water will be pumped through the filter using a peristaltic pump. Tubing will be acid-cleaned Teflon, except for the small amount of tubing within the pump apparatus, which will be acid-cleaned silicone tubing. One or more liters of water will be pumped through the filter, the exact volume being recorded. The filter will be removed and placed in a clean Teflon vial placed in a polyethylene bag. Filters will be frozen as soon as possible after collection. Additional particulate collections will be stored for duplicates (and for methyl mercury analysis).

Appropriate QA/QC procedures will be adopted during field samples. The QC requirements are detailed in the previous section and details of QA related issues are in Appendix 1.

Samples will be stored frozen on board and will be shipped overnight to the University of Maryland by Federal express in particle-free plastic boxes soon after arrival in port. A maximum interval of two months is expected between sample collection and completion of analysis. However, samples have been successfully stored for six months by other investigators without loss (Hurley, pers. comm.). Thus, if a holding time of six months is exceeded and no evidence to support a longer interval is provided, the sample data will be qualified as estimated. Field labels are attached to the Go-Flo bottles as soon as possible after retrieval. This label will have an ID number that will be used as the primary control number for chain of custody. This ID number will be attached to the outer bag of the Teflon bottle etc. See chain of custody section below. The only calibration required is for the winch as the depth is determined from the "line out" record of the winch operator. The calibration of the winch is monitored by the ship personnel.

Teflon equipment will be cleaned in concentrated HNO_3 (ACS Reagent grade) for a week and rinsed with deionized water. Bottles will then be filled with 10% acid and will be kept for a week. After further MilliQ rinsing, bottles will be filled with 1% HCl and this dilute acid will remain in the bottles until samples are collected. Samples will be dispensed in the clean room into 2 L Teflon bottles as described above.

Appendix 1.

Field Sampling Protocols (from QAPJP)

1.0 Preparation of Sampling Bottles and Subsequent Collection of Mercury in Open Waters

This SOP is intended to provide a step by step procedure for the preparation of samplers and sample bottles necessary for the collection of contamination-free water samples from depth in open water environments, and for the collection methods to be employed in the sample collection.

1.1 Overview

Samples collected for mercury analysis form part of the LMMB study and the data will be used to constrain a mass balance for mercury in Lake Michigan. The samplers used in the collection of samples are specially designed Teflon-lined Go-Flo bottles, manufactured by General Oceanics. The bottles are able to be remotely triggered using a Teflon-coated metal "messenger" and thus can be used to collect samples at any pre-determined depth in the water column. The bottles are deployed attached to a non-metallic Kevlar line to ensure that the sampling apparatus does not lead to sample contamination. Procedures are designed to ensure that the Go-Flo bottles do not leach mercury into the sample water during deployment, recovery and before decanting of samples into specially prepared Teflon bottles. All bottles are kept in plastic bags when not in the clean room or in use to minimize contamination. Personnel handling the Go-Flo bottles need to wear plastic gloves and to avoid contact with the ball valves and internal parts of the Go-Flo bottles. All precaution is required if uncompromised samples are to be obtained. The Go-Flo bottles should never be placed directly on the deck or any hard surface otherwise foreign particles might be lodged in the plastic ball valves leading to subsequent contamination.

1.2 Go-Flo Bottle Preparation

Newly purchased Go-Flo bottles are first checked for obvious defects and the closing and opening mechanisms checked. The bottles are then rinsed and scrubbed, using a soft brush, with soapy water to remove any loose particles from inside or outside the bottle. The mechanism of the ball valves is removed and the bottle O-ring removed and washed. The components are then rinsed with deionized water. The bottle is then re-assembled. The bottles are then soaked in a weak 0.05% HCl solution for a week - this is done by placing the bottle in a plastic garbage pail that has been lined with a clean polyethylene bag. The ball valves are rotated periodically to ensure that all parts of the ball valve that could contact the sample water after the bottles are closed is cleaned. The bottle is then rinsed with MilliQ water and filled with water and allowed to stand for six hours with the balls in the closed position. A sample of the MilliQ water is taken for later comparison with the water concentration in the bottle after 6 hours of leaching. After six hours the water in the Go-Flo bottle is sampled and analyzed, along with the initial sample. Any significant increase in concentration (>15%) will suggest that the bottle is still contaminated and leaching mercury. If so, the bottle will be re-cleaned using the procedure above.

1.3 Teflon Bottle Preparation and Handling

All sample bottles used for sample collection are constructed of Teflon as this has been found to be the material that results in the least contamination of samples, after the bottles have been rigorously cleaned. New Teflon bottles are washed with soapy water, and then with acetone to remove any organic residues. The bottles are then leached with concentrated HNO_3 (ACS Reagent grade) for a week. After being rinsed with deionized water, bottles are then be filled with 10% acid and will be kept for a week. After further MilliQ rinsing, bottles will be filled with 1% HCl and this dilute acid will remain in the bottles until samples are collected. Bottles are hermetically sealed (i.e. the caps are wrenched tight using a wrench whose metal parts have been covered with several layers of plastic) at this point and stored and transported within two poly ziplock bags. The bottles are packed into a large poly bag and are typically transported in plastic coolers. On board, the coolers will be opened in the ante room of the clean room. When the bottles are removed from the coolers, the outer bag is removed and the bottle is taken into the clean room. Samples will be dispensed in the clean room from the Go-Flo bottles into the Teflon bottles as described below. Just prior to sample decanting, the Teflon bottles will be unbagged, emptied of their acid solution and rinsed with MilliQ water. Strict clean techniques will be used in the collection and decanting of samples, i.e. gloves are worn at all times and are changed whenever the personnel switch from handling "clean" and "dirty" things e.g. outer poly bags are considered dirty, inner bags clean; all things within the clean room are considered clean, otherwise they should not be inside.

1.4 Sample Collection

The samples are collected using a "hydrowire" deployment system, with Kevlar as the wire. The non-metallic weight, which is stored in a plastic bag in-between sampling events, is first attached to the end of the wire. The weight is lifted overboard by the winch operator and lowered until it is in the water. At least 10 m of wire should be extended prior to Go-flo bottle attachment. Prior to sampling, Go-Flo bottles should be moved to the ante room of the clean room, or a suitably clean environment closer to the deployment site, and placed in a container for easy access. The bottles are still bagged at this stage. The Go-Flo bottles are "pre-cocked" in the clean room. Details of the cocking methods are contained in the manual that is supplied with the Go-flo bottles. Briefly, the ball valve is rotated so that the string parts of the Go-Flo can be attached to the plunger mechanism. Throughout the whole cocking procedure, the Go-Flo should be either placed on a plastic covering on the floor or be hand-held. The pressure release valve is pulled out and the plastic balls on the string positioned around the valve. The "bungie cord" attached to the ball valve is then rotated back so that both the string and the cord are under tension. The cocking should be checked to ensure that it has been correctly cocked. Pushing the pressure release valve should cause the balls valves to move to the open position. Pressing the plunger should then release the string and result in the closure of the bottle. Recock the bottle after this check in a similar manner. The cocked bottle is then placed in poly bags and removed to the ante room and placed in the bottle container. The bottles are individually unbagged when required, and are carried by gloved personnel to the deployment site. The bottle is attached to the line by the person carrying the bottle with additional help, if required. The bottle is then lowered down into the water and slowly lowered to about 20 m. As the pressure release valve opens the Go-Flo underwater, a parcel of air is released to the surface. The bubbles are typically easily seen, and this is indicative that the bottle is open. If, on the rare occasion that bubbles are not seen, there is a concern that the bottle has not opened - this again is not the typical scenario - the bottle can be raised slowly so that

personnel looking over the side of the ship can look and see if the bottle is open. This, of course, is only feasible in clear water as it is undesirable, from a contamination standpoint, to bring the bottle to the surface. If the water is unclear or rough, it is better to just assume the bottle is open and accept the associated risk i.e. a redeployment. The weight of the retrieved bottle will be indicative of it being empty or filled with water. The bottle is lowered to the correct depth and then the messenger is attached to the line and released. The messenger will trigger the bottle and it can then be retrieved to the surface. Adequate time, based on the time required for the messenger to reach the bottle must be allowed before retrieval. When the bottle is retrieved to deck level, the person who attached the bottle will disengage it and carry it, without putting it down or touching the ship's parts to the box and replaced it in the plastic bags. The Go-Flo bottle is then taken into the cleanroom as soon as possible. The Go-Flo bottles can be deployed singularly or a string of bottles can be deployed at the same time, depending on the circumstance.

1.5 Sample Decanting and Labeling

The Go-Flo bottle is taken into the clean room and placed on the bench, on a plastic bag, in the upright position. Personnel should put on clean gloves at this point. The air release valve is opened and the sample is decanted into the rinsed and ready Teflon bottles. About 20 mL of water is decanted into the Teflon bottle, and the bottle rinsed. The sample is then decanted. As the samples will be frozen, the bottles should only be filled to the beginning of the neck to allow for the expansion of the water on freezing. If insufficient airspace is left, samples can leak or, if the bottle is very tightly sealed, the bottle can split. After filling, the bottle cap is immediately replaced and any additional samples taken. After all samples are taken, the caps of the Teflon bottles are wrenched tight using a plastic coated wrench. The bottles are then double-bagged, and taken to the freezer for storage. The information on station #, depth, collection date, Go-Flo #, and ID # will be entered into the data sheet.

Date

ID#

Station #

Depth (m)

Go-Flo #

Bottle #

Vol. (L)

As # H₂O Analy.

Hg-T Analy.

SHIPPED BY:

Box #

RECEIVED BY:

Date:

Notes: 1) The ID # will consist of the date, station, and depth.