A. Scope:

This method pertains to the collection of ambient (or other "low level") water samples for subsequent determination of trace amounts of metals. This method is applicable for the determination of concentrations of the following metals: Antimony, Arsenic, Cadmium, Chromium (III), Chromium (VI), Copper, Lead, Mercury, Nickel, Selenium, Silver, Thallium, Zinc and other metals, metals species, and elements amenable to determination at trace levels. This method is not intended for determination of metals at concentrations normally found in high levels from untreated discharges from industrial and/or municipal facilities.

The ease of contaminating ambient water samples with the metal(s) of interest and interfering substances cannot be overemphasized. This method employs sampling techniques that should maximize the ability of the sampling team to collect samples reliably and eliminate sample contamination and is based on US EPA Method 1669. Feel free to contact the lab with questions before sampling (608-224-6202).

B. Summary of method:

Prior to sample collection low level metals sampling kits need to be ordered from the SLOH. All sampling equipment and sample containers must be rigorously cleaned in a laboratory or cleaning facility using detergent, dilute mineral acids (i.e. nitric or hydrochloric acid), and reagent grade water. For most sampling events the sample bottles will come cleaned and prepared by the Wisconsin State Laboratory of Hygiene ready for field use.

While it may be possible to collect the samples solo, it is highly recommended that the sampling occur with a two person team. Upon arrival at the sampling site, one member of the two person sampling team is designated as "dirty hands"; the second member is designated as "clean hands". All operations involving contact with the sample bottle and sample collection device are handled by the individual designated as "clean hands". "Dirty hands" is responsible for preparation of the sampler (except the sample container itself), operation of any machinery, and for all other activities that do not involve direct contact with the sample. All sampling equipment and sample containers used for metals determinations at "low- levels" must be non-metallic and free from any material that may contain metals. Sampling personnel are required to wear clean (new), non-talc gloves at all times when handling sampling equipment and sample containers. Sampling should NOT occur through ice if a metallic instrument is required to make a hole through the ice to reach surface water.

1. Standard QA/QC practices

At least one field blank should be processed per site once every two years for trend analysis, or in conjunction with every 8 to 10 samples, whichever is more frequent. Reagent-grade (Type I) water should be transported to the sampling site and processed, preserved and stored on-site, in the same manner as the surface water sample. At sites where low level metals are detected above the water quality standards it is recommended that the field blanks be done at least annually. For additional QAQC, a cleaned Teflon bottle containing reagent-grade water should be transported to the field to be used as a "trip blank". This will allow the user to determine of the source of

contamination is from on-site sample processing or laboratory bottle cleaning/reagent-grad water contamination.

In addition to processing field blanks at each site, a field duplicate must be collected at each sampling site once every two years for trend analysis or in conjunction with every 8 to 10 samples, whichever is more frequent. At sites where low level metals are detected above the acute or chronic water quality criteria it is recommended that field duplicates be done at least annually. Low-level metal(s) sampling QAQC procedures may deviate from this plan based on project specific QAPPs, but it is highly recommended that the above procedures are followed at a minimum.

C. Safety:

Safety precautions of a general nature should be recognized. Life jackets should be worn if sampling from a boat or in areas of swift current. Collecting samples in cold weather, especially around cold waterbodies, carries the risk of hypothermia and collecting samples in extremely hot and humid weather carries the risk of dehydration and heat stroke. This sampling technique may call for the wearing of non-standard clothing, and therefore precautions should be taking to account for the existing temperature and general climate.

D. Equipment:

All sampling equipment and sample containers should be pre-cleaned and pre-packaged in a laboratory or cleaning facility. To minimize difficulties in sampling, equipment should be packaged and arranged to minimize field preparation and unnecessary handling of cleaned equipment. Materials such as gloves, storage bags, and wraps may be used new without additional cleaning unless the result of a blank identifies any of these materials as a source of contamination. Equipment should be stored and transported in a manner which will minimize or eliminate potential for contamination of the sampling equipment.

Appropriate sample bottles will be determined by ongoing research or monitoring. A certified laboratory can aid in deciding sample bottle material (polyethylene, Teflon, etc.). Teflon sample bottles (after cleaning) will provide a clean bottle that will introduce insignificant levels of heavy metals to the sample and are considered the standard bottle material type. However, while Teflon (the Teflon should either be FEP or LDPE) bottles may be used repeatedly, they are relatively expensive. An alternative is to use polyethylene sample bottles. Polyethylene bottles may be less reliably clean, and in most cases, are not suitable for the collection of samples for low-level mercury analysis. If polyethylene bottles are to be used, the laboratory at which the samples will be analyzed should be consulted.

Gloves should be constructed of non-talc polyethylene, latex, nitrile, or vinyl. Shoulder-length gloves are needed if samples are to be collected by direct submersion of the sample bottle in the water. Storage bags should be new, zip-type, colorless polyethylene. Coolers used for sample transport should be clean, and non-metallic. Sampling personnel should wear a lint-free garment which can be a "moon-suit" made of Tyvek, or equivalent lint-free clothing such as a clean wind-breaker, gortex, etc. If hip-boots or chest-waders are to be worn, they should be clean and free from debris such as sediment "muck", dust, etc. If possible, the waders/boots should be dedicated to clean metals sampling. E.

Interferences and Special Precautions:

There are numerous routes by which samples may become contaminated. Potential sources of trace metals contamination during sampling include: metallic or metal-containing sampling equipment, containers, labware (e.g. talc gloves that contain high levels of zinc), reagents, and deionized water; improperly cleaned and stored equipment, labware, and reagents; and atmospheric inputs such as dirt and dust from automobile exhaust, smoke, nearby roads, bridges, wires, poles, etc. Human contact can be a significant source of trace metal contamination. For example, it has been demonstrated that dental work (e.g., mercury amalgam fillings) can contaminate samples that are directly exposed to exhaled air. Carry-over contamination can be minimized and controlled by keeping equipment clean, beginning sample collections at the probable lowest concentration site, using field blanks, and rinsing equipment with reagent grade water or dilute acid following collection(s).

F. Collection Procedures:

Whenever possible, samples should be collected facing upstream and upwind to minimize introduction of contamination. Samples may be collected while working from a boat (cleaned and non-metal) or while on land (or in stream). Surface samples are collected by using a grab sampling technique. The principle of the technique is to immerse the sample bottle before opening or closing. Not only will air-borne contaminants be avoided, but surface films and other debris entering the sample bottle will also be minimized.

The sampling team should ideally approach the site from down current and downwind in order to prevent contamination of the sample by particles sloughing off the boat or equipment. Approaching from downstream is more important than downwind, but if both are attainable, contamination potential would be minimized. If sampling from a boat great care should be taken to always work up-stream and off the bow of the boat. All operations involving contact with the sample bottle should be done by the individual designated as "clean- hands". "Dirty-hands" is responsible for all activities that do not involve direct contact with the sample. Initially, this appears to be clear-cut and straight forward; however, it can be tedious as there are many functions to perform. The sampling team should plan accordingly. Only samples for dissolved metals are field filtered. This process can introduce contamination and should be always be accompanied by a field filtered blank. If the sample is to be filtered, all actions pertaining to the filtration should occur in the cleanest location attainable. This may be an improvised glove-box in the field. In some cases, if the elapsed time is minimized, filtration can occur in the laboratory after sample transport. Any filtration equipment must be very rigorously cleaned and stored/transported in a manner consistent with "clean-sampling".

Extreme care must be taken during all sampling operations to minimize exposure of the sample to human, atmospheric, and other sources of contamination. Care must be taken to avoid breathing directly on/in the sample, and whenever possible, the sample bottle should be opened, filled, and closed while submerged. Clean samples can be obtained during precipitation events; however, more care must be taken to avoid contact of the sample with the precipitation, and other atmospherically derived contamination.

1. Manual collection of surface samples (grab samples)

a. At the site, the sampling team should put on their "moon-suits", windsuits, etc. All sampling personnel must put on clean gloves prior to commencing sample collection activity, with "clean-hands" donning shoulder-length gloves.

b. "Dirty-hands" must open the cooler or storage container, remove the double bagged sample bottle from storage, and unzip the outer bag.

c. Next, "clean-hands" opens the inside bag containing the sample bottle, removes the bottle, and reseals the inner bag. "Dirty-hands" then reseals the outer bag.

d. "Clean-hands" then proceeds to sample collection. If the sample bottle was transported with dilute acid, "clean-hands" unscrews the cap and, while holding the cap upside down or completely covered in palm of hand, empties the dilute acid solution from the bottle. Bottle is re-capped. If the bottle was transported empty/dry, "clean-hands" proceeds to the water to be sampled.

e. "Clean-hands" submerges the sample bottle (while capped), unscrews the cap and allows the bottle to fill with sample. "Clean-hands" screws the cap on the bottle, raises the bottle above water surface and empties the rinsate downstream. After three rinses, "clean-hands" fills the bottle under water and allows the bottle to fill with sample. After the bottle has filled, and while the bottle is still submerged so that the mouth of the bottle is underwater, "clean- hands" replaces the cap of the bottle. In this way, the sample has minimal contact with ambient air. After collection of the sample, the sample should be visually inspected to determine whether any unrepresentative debris has been collected in the bottle. Examples of foreign debris include: insects, leafy matter, and other "macro-particles". Debris such as algae or suspended sediment that is uniform or representative of the river is acceptable in the sample bottle. If foreign matter is in the bottle, the sample should be recollected using the same procedure and equipment.

f. "Dirty-hands" re-opens the outer plastic bag, and "clean-hands" opens the inside bag, places the bottle inside it, and zips the inner bag.

g. "Dirty-hands" zips the outer bag and stores the bottle.

h. At this time, after each sample is collected, the sample number is documented in the sampling log, and any unusual observations concerning the sample and the sampling are documented. The sample will be acidified by the certified lab on arrival at the laboratory and not by field personnel. If samples are to be collected with a grab sampling device, all efforts must be taken to ensure cleanliness. Any apparatus used must be constructed of appropriate materials - Polyethylene or in some cases, Teflon is preferred. If any devices are used, care should be taken to decontaminate the apparatus prior to subsequent use. This should, at a minimum, include rinsing with reagent grade water or dilute nitric acid solution.

2. Manual collection of surface samples (grab samples) from a boat

Sampling from a boat presents other challenges for remaining "clean". Because of the various types of circumstances which may be present, it is difficult to address all of them. In general, all sample handling should occur while in the boat. Life preservers should be worn underneath any "clean clothing" when possible. As always, judgment must be used to ascertain those precautions which are applicable either for safety, or for obtaining a clean sample. The boat must be non-metal, and cleaned for removal of debris or other obvious sources of contamination. It is normally not necessary to "acid-clean" a boat, or to undertake other extreme measures. However, care must be taken to at least "wipe off" the outside surfaces of the boat. Temporary single-use "clean" surfaces can be created by putting down fresh, never-used, sheets of clear plastic or clear bags on top of coolers or bins.

Similar precautions should be taken to minimize contamination of the sample by approaching the sampling location from downstream (especially in a boat) and/or downwind. Gasoline engines should be avoided virtually at all cost as the exhaust and fuel sources can very easily compromise the sample integrity. Electric motors can be used if precautions are taken to isolate the battery and any other related components of the motor.

3. Sampling at Depth

When depth sampling is performed it is very easy to compromise the cleanliness of a sample as more hardware is involved in obtaining a sample (lake, nonwadeable river, etc.). One way to do this is to use rigorously cleaned Teflon tubing with a peristaltic pump. The pump-tubing section is a common source of contamination and must be considered carefully. Special care must be taken to clean/leach the short section of tubing passing through the pump-head. The water can then be pumped to a boat or to shore for sample collection. "Clean-hands/dirty-hands" protocol must be followed during this procedure, and since the bottle will be open to the atmosphere, care must be taken to limit introduction of airborne particulates, etc. For example, do not leave a bottle open for extended periods of time as this may introduce air borne contaminates.

G. Special Handling and Preservation:

Special handling precautions have been discussed in Section "F" but under certain situations field preservation and filtering may be required. If field preservation is required, preservation should be performed in a clean environment using ultrapure grade acid supplied by the lab. Plain reagent grade acid should never be used for acidification of trace metal samples since this will contaminate the sample. It is best to leave acid preservation for the laboratory to do. Indicate on the paperwork the preservation status of the sample so the laboratory knows they must add acid. If preservation must be done in the field, acidify samples in an environment as clean as possible. All actions should be taken with gloved hands, using clean-hand/dirty-hands techniques and as rapidly as possible to preclude particulates from contaminating the sample. If field filtration is needed it must be completed before sample is acid-preserved.

H. Sample Labeling:

Because of difficult nature of obtaining clean samples, sample labeling can be a source of sample contamination via human contact with the label and the sample. If the bottle must be labeled directly, they can be etched prior to cleaning. Almost all WSLH bottles are etched with a alpha-numeric code, sometimes not visible until the bottle is removed from the bags. Otherwise, it is usually easier to label the outer (of the two) plastic bags with a marker ("sharpie"). It is also easiest to write on the outer bag while it is dry. An excellent time to do this is for "dirty hands" to label the bag while he/she is waiting for "clean hands" to take the sample.

I. Documentation:

Standard documentation procedures should be followed for the collection of samples for low-level heavy metal analysis. However, it must be very clear that the laboratory is aware that the samples were collected using "clean techniques" and whether acid preservation took place in the field or not. Otherwise, it is possible that the laboratory would open the samples or otherwise expose them to conditions that could compromise the sample integrity. Before sample submission to the lab, also confirm that the labeling on the outer bags corresponds to what is recorded on the sample test request forms.

J. Decontamination:

All efforts must be made to keep all applicable sampling equipment clean and stored properly. Decontamination should occur very shortly after field sampling is completed (sometimes decontamination in the field is preferable). If waders or other equipment is used, extra care should be exercised to keep the materials cleaned and otherwise kept in a location where everything will remain free from contaminating material. In some cases, it may prove useful to rinse equipment with clean water, or dilute acid to further ensure clean equipment. Any reusable equipment should be thoroughly cleaned and stored in a manner to prevent contamination.

K. SOP updates tracking

Version Number	Date	Sections	Name	Approval
2.4	11/12/13	All	Shupryt/Turcotte/ Arneson/Gorski/Skaar	Mike Shupryt, 3/26/2015
2.5	8/30/2018	B.1	Shupryt	Shupryt

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WDNR PUB-WY-022-2015