

Ambient Metals Project Proposal

Final Quality Assurance Project Plan

by
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Washington State Department of Ecology
Environmental Investigations and Laboratory Services Program
Ambient Monitoring Section

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PROJECT DESCRIPTION

Overview

The current Washington State metals criteria (WAC 173-201A-060) are EPA derived, empirically based calculations using acute and chronic bioassay information. A difficulty in applying some of these chronic criteria (specifically cadmium, copper, lead, and mercury) is the limitations of the EPA-acceptable analytical methods. It is possible to have chronic criteria near or even below the detection limit of the acceptable analytical methods. This creates problems when data near detection limits is compared to the chronic criteria. The regulatory requirements allow the development of new analytical methods to address these limitations, but these new methods must be approved by the department and subsequently EPA.

Sixty-one freshwater water body segments were considered for listing in the draft 1994 303(d) list based on potential metal problems. These 61 freshwater segments are listed in Appendix A. This preliminary list was derived by comparing total recoverable metals information from a variety of sources to total recoverable water quality criteria. With the adoption of new dissolved criteria for most metals in 1992, most of the stations initially listed for consideration will be removed by default because little data exists on the ambient concentrations of dissolved metals. Of the 61 originally listed for consideration for the 1994 303(d) list, only 10 will remain (Ecology, 1994). These 10 are shown in Appendix A with bold type. The lack of data on the concentration of dissolved metals at 48 of the 51 remaining stations could potentially result in the removal of stations that do have metal problems. Removal of 3 of the 51 stations (WA-55-1010, Little Spokane River; WA-54-1020, Spokane River; and WA-CR-1010, lower Columbia River) has been demonstrated as being warranted based on 1991 or newer dissolved data. For more information, see Appendix B - Supporting Information.

Pilot Methods Study

A comparative study was conducted in 1992 and 1993 to determine if the ambient monitoring field techniques could generate low level metals information. That study was designed to:

- 1) compare grab sample collection methods (grab samples versus self-closing sampler), and
- 2) quantify the total variability (total variability = in-stream + analytical + field processing) in low level metal results.

From November 1992 to May 1993, the Toxic Investigations Section (TIS) and the Ambient Monitoring Section (AMS) of the Environmental Investigations and Laboratory Services Program (EILS) jointly collected bi-monthly water samples at three locations, each using separate methods. TIS staff collected their water samples using a wading grab technique and AMS staff a bridge deployed sampler. Field processing, and laboratory analysis were identical. A description of this project and a discussion of the results is included as Appendix C of this report. The findings of the methods comparison study suggests the AMS methods and sampler are adequate for the collection of low level metal information.

Project Objectives

The goal of this project is to obtain low-level ambient metals and hardness data from rivers and streams in Washington. Specific objectives are to:

- 1) provide background dissolved and total recoverable metals concentrations in support of Ecology's water quality based permitting.
- 2) provide dissolved and total recoverable metals information for rivers and streams within Washington for the 1996 305(b) evaluation; and
- 3) decide if the removal of 48 freshwater water bodies from the 1994 preliminary 303(d) list is supported by in-stream dissolved metals concentrations;

Sampling Design

To meet the proposed objectives this project consists of two tasks. The first task establishes background metals concentrations and provides metals information to compare to Ecology's new dissolved metals criteria. The second addresses the issue of station removal from the draft 303(d) list.

Task 1: Ambient Metals Concentration

To obtain metals and hardness data to compare with Washington State's Water Quality Standards and to establish background information for the permitting process, AMS will collect bi-monthly water quality samples at the 10 ambient monitoring stations indicated in Figure 1 and listed in Table 1. These stations will also be monitored for conventional parameters in Wateryear (WY) 1995. Sample collection will be conducted mid-channel off a bridge, wherever possible, or by wading. Metals analyses are listed in Table 2.

Task 2: Metals Screening at Locations Removed from the WY 1994 303(d) List

To determine whether the decision to drop 48 waterbodies for the 1994 303(d) list was valid, AMS will collect at least the minimum data required for listing (two samples at least 48 hours apart). We will collect one sample during a high flow month (April/May) and one during a low flow month (August/September). Sample sites will be located within the water segment listed in the draft 1994 303(d) list (Appendix B). Figure 1 shows the approximate locations of the rivers and streams to be sampled as part of this task. Three of the 48 water segments will be monitored under Task 1 described above. Water samples will be collected from mid-channel off a bridge, wherever possible, or by wading. Sample analysis will include the metals listed in Table 2.

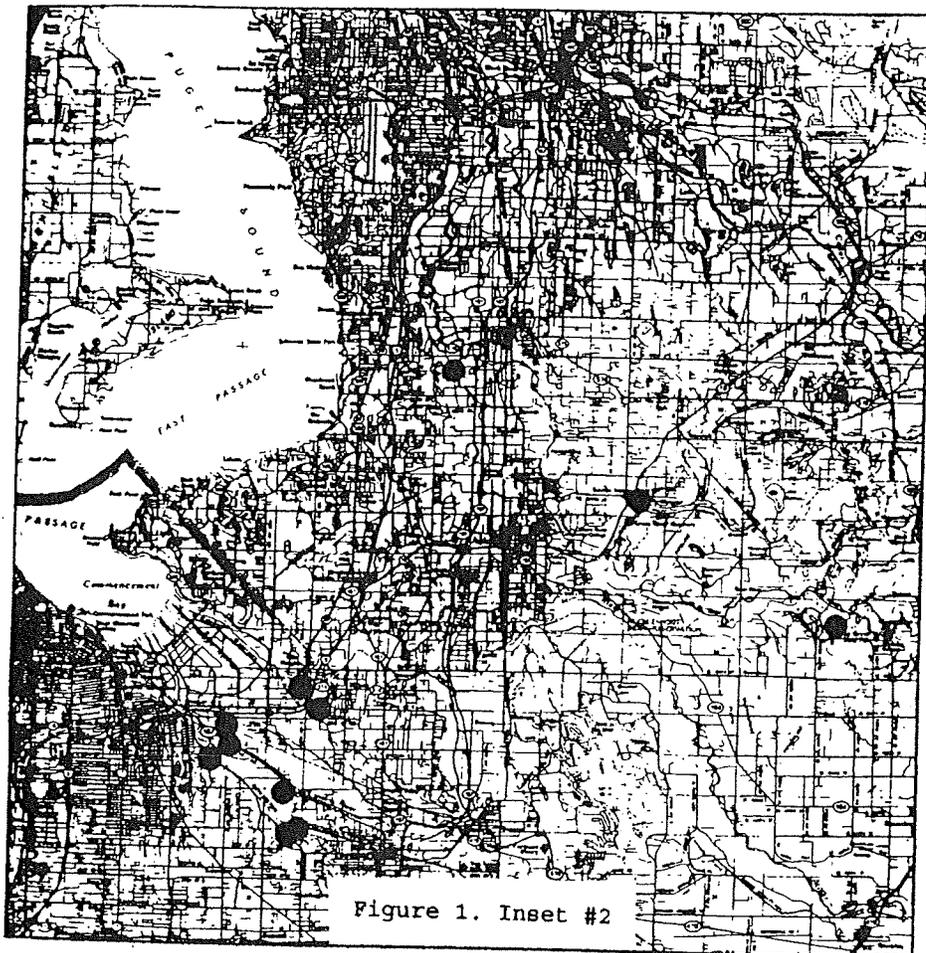
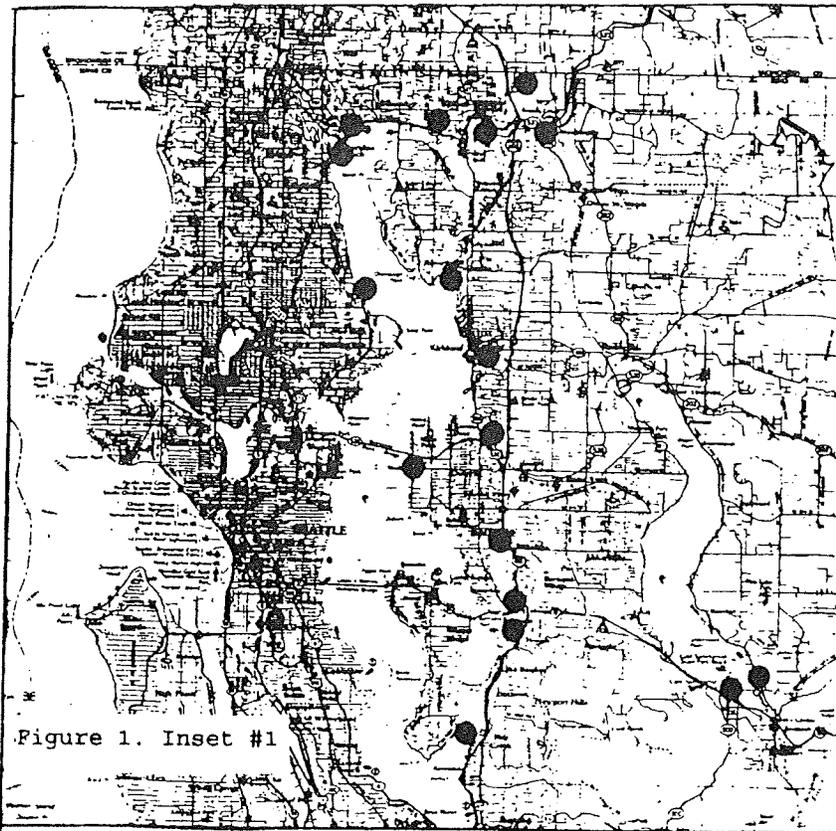


Figure 1a. Insets to Figure 1.

Table 1. Existing ambient monitoring location where metals and hardness will be added to the parameter list.

Station Number	Station Name	Station Type
1) 03A060	Skagit River near Mount Vernon	Core
2) 05A070	Stillaguamish River near Silvana	Core
3) 04A100	Skagit River @ Marblemount	Bench Mark
4) 10A070	Puyallup River @ Meridian Street Bridge	Core
5) 26B070	Cowlitz River @ Kelso	Core
6) 30A060	Columbia River below the Dalles	Rotating
7) 31A070	Columbia River @ Umatilla	Core
8) 52A110	Sanpoil River 13 miles below Republic	Rotating
9) 57A150	Spokane River @ Stateline Bridge	Core
10) 61A070	Columbia River @ Northport	Core

Table 2. Metals analyzed as part of the Ambient Monitoring Section's Metals Study and the proposed detection limits ($\mu\text{g/L}$).

Parameter	Chronic Criteria 25 mg/L Hard	Current ^a Reporting Limits	Required Detection Limits	SRM ^b SLRS-2
Total Recoverable				
Arsenic (As)	190 ^c	30.0 ^d	30	0.77 \pm 0.09
Chromium (Cr)	66.5	5.0 ^d	5.0	0.45 \pm 0.07
Mercury (Hg)	0.012 ^c	0.010	0.001	
Dissolved				
Cadmium (Cd)	0.330	0.1	0.03	0.028 \pm 0.004
Copper (Cu)	3.12	0.05	0.03	2.76 \pm 0.17
Lead (Pb)	0.374	0.374	0.04	0.129 \pm 0.011
Nickel (Ni)	46.36	4.0	4.0	1.03 \pm 0.10
Zinc (Zn)	29.18	3.0	3.0	3.33 \pm 0.15

^a Reporting limits are a function of IDL, Analytical and blank results (Kammin, 1994)

^b Canada River Water Standard Reference Material (SLRS-2)

^c Not hardness-based criteria

^d ICP detection limit

Schedule

Field Work:

Manchester MDL Study	April 1994
303(d) Stations (High Flow)	April/May 1994
Ambient Metals	Bi-monthly (May 1994-March 1995)
Manchester MDL Study	September 1994
303(d) Stations (Low Flow)	September 1994
Manchester MDL Study	March 1995

Draft Report:

303(d)	March 1995
Ambient Metals	June 1995

Final Report:

303(d)	April 1995
Ambient Metals	August 1995

Project Organization and Responsibility

Client:	Water Quality Program
Project Lead:	Brad Hopkins
Sampling Personnel:	Bill Ehinger, Dave Hallock, Brad Hopkins and Rob Plotnikoff
Field QA Review:	Brad Hopkins
Analytical Services:	Ecology Manchester Laboratory
Laboratory QA Review:	Bill Kammin
Cost:	\$ 126,530

DATA QUALITY OBJECTIVES

Data generated in this project will be used to meet three primary functions. The first will be to determine if the removal of the 48 locations from the draft 1994 303(d) list is supported by in-stream water quality. Second is to establish background metals concentrations for Ecology's water quality-based permitting at select locations. The final function is to provide low level metals information that can be compared to the updated water quality standards. To meet these needs the data should meet the following conditions for precision, detection limits, bias, representativeness, completeness, and comparability.

Precision

Total precision of field replicates/splits should be less than 20% Relative Standard Deviation (RSD) (see Summary of Calculations page 17). Laboratory precision (% RSD) at the chronic criteria should ideally be at or near 5% (Ecology, 1991). However, if laboratory precision is above 5% RSD the appropriate data qualifier will be assigned (see Data Management).

Detection Limits

The preferred detection limits for most metals are at least one order of magnitude below the chronic criteria. Table 2 lists the preferred detection limits and the chronic criteria (based on a hardness of 25, where applicable). Given the analytical limitation for some metals analysis methods (Pb and Cd specifically), the required detection limits may not be attainable. If the required detection limits can not be met, the analytical detection limit should be no higher than the chronic criteria listed in Table 2.

Bias

Laboratory bias should be < 10% (see Summary of Calculations)

Representativeness

The following are the sampling schemes designed to ensure the data are as representative as possible given the constraints within the project.

Task 1: Ambient Metals Concentrations

Statewide ambient metals concentrations (Task 1) will be addressed by adding selected metals to the parameter list of ten existing ambient stations listed in Table 1. The station selection was based on concerns expressed by Department of Ecology staff as part of the Wateryear 1994 Watershed Needs Assessments. Due to budget constraints, metals will be analyzed bi-monthly instead of monthly as with conventional parameters (see Sample Design).

Task 2: Metals Screening at Locations Removed from the WY 1994 303(d) List

Samples to address Task 2 of this project will be collected under both high flow (April/May) and low flow (August/September) conditions at locations within the waterbody to be listed (see Sample Design).

Completeness

Task 1: Ambient Metals Concentrations

Weather conditions and laboratory sample load are the only situations that could alter the project schedule as outlined above. Missed sampling events or compromised data sets will not be re-sampled.

Task 2: Metals Screening at Locations Removed from the WY 1994 303(d) List

It is critical to the success of the project to meet the minimum data requirement for listing a location on the 303 (d) list (two samples at least 48 hours apart). If for any reason the data sets are compromised, the station(s) will be resampled. Ideally, this project is designed to address the concentrations of select metals under both high flow and low flow conditions. However, it is more important to have two complete data sets to compare to state water quality standards than to stick rigidly to a specific flow regime.

Comparability

The pilot method study was completed to address concerns about data comparability. The findings of this study suggest the AMS method and sampler are adequate for ultra trace metals determination. However, it should be noted that the lack of comparable historical data is the primary reason for the inception of this project.

SAMPLING PROCEDURES

The following section provides information on the cleaning procedures, sample collection, and field processing techniques for this project.

Cleaning Procedures

Cleaning procedures for sample bottles and filter units are discussed in Appendix D Manchester Environmental Laboratory Standard Operating Procedure for the Laboratory Clean Room (MELSOP).

Sample Bottles

The cleaning procedure for Teflon® bottles and vials can be found in Appendix D, Section 4.1 and 4.3, respectively.

Filter Units

A 0.45 μm cellulose nitrate filter unit, shown in Figure 2, (Nalgene #450-0045, type S) will be precleaned following the procedure established in Appendix D, Section 4.2.

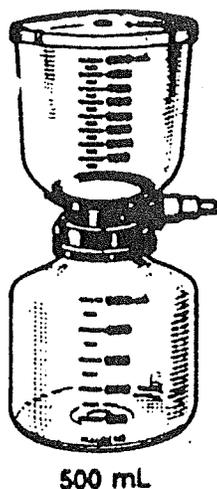


Figure 2. Filter apparatus for dissolved metals.

Sample Collection

All water samples will be collected as a whole water single grab directly in 500 mL Teflon® bottles. Water samples will be collected with the stainless steel and Teflon® sampler shown in Figure 3. The sampler will be lowered from a bridge to the water surface and allowed to orient itself so the bottle is upstream. Once submerged, the sampler will open the bottle approximately 25 cm under the surface of the water. As the sampler is lifted from the river the bottle is automatically recapped. If sampling from a bridge is not practical, the sample will be collected directly in the sample bottle by wading into the stream and submerging the stainless steel sampler.

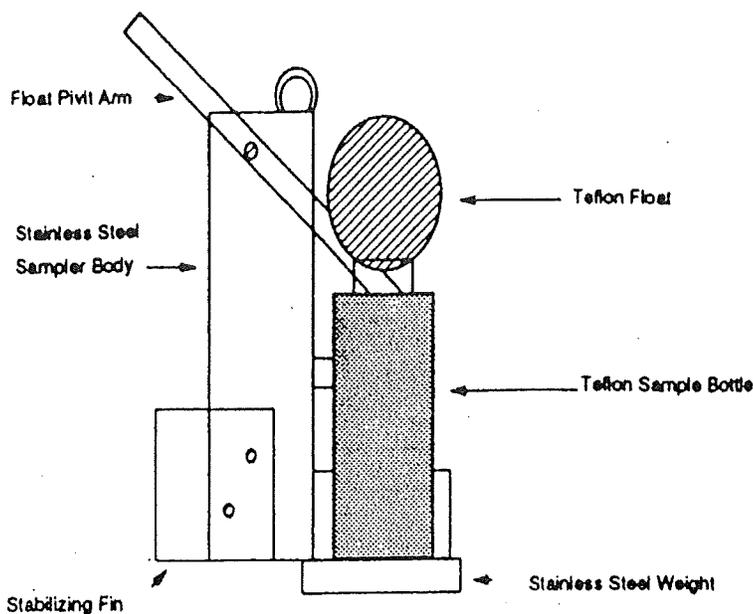


Figure 3. Stainless steel metals sampler.

Field Processing

Dissolved Metals

Samples for dissolved metals will be vacuum-filtered in the field through a disposable filter shown in Figure 2. The filtered water sample will be transferred to a clean Teflon® bottle. A pre-measured volume of acid (5 mL of 1:1 sub-boiled Concentrated Nitric Acid + deionized water) transported in a small Teflon® vial will be added (one per sample). Each sample bottle will then be placed in a polyethylene bag and iced for transport to the MEL.

Total Recoverable Metals

Samples for total recoverable metals will be acidified (5 mL of 1:1 sub-boiled Concentrated Nitric Acid + deionized water) by adding a pre-measured volume of acid from a small Teflon® vial (one per sample) directly into the container used to collect the sample. Each sample will then be placed in a polyethylene bag and iced for transport to the MEL.

LABORATORY ANALYSIS

Water samples will be analyzed for the dissolved and total recoverable metals listed in Table 2. Where applicable, EPA Contract Laboratory Program (CLP) requirements will be met.

Dissolved Metals

Dissolved metals will be analyzed at Ecology's MEL using inductive coupled plasma - mass spectrometry (ICP-MS) (a modified version of EPA Method 200.8).

Total Recoverable Metals

Total recoverable metals will be analyzed at Ecology's MEL using microwave assisted digestion (EPA Method 202.2) and ICP (a modified version of EPA Method 200.7). The ICP method does have a higher detection limit (Detection Limits for As ICP = 30 $\mu\text{g/L}$ ICP-MS = 0.5 $\mu\text{g/L}$ and Cr ICP = 5 $\mu\text{g/L}$ ICP-MS = 0.1 $\mu\text{g/L}$) but the relatively high chronic criteria for As and Cr (190 and 66.5 at a hardness of 25, respectively) makes the extra cost of ultra low level metals work unwarranted. Mercury will be determined using the Free Bromide Digestion (EPA Method 245.7) and Cold Vapor Fluorescence (EPA Method 245.1).

DATA ASSESSMENT PROCEDURES

Laboratory Evaluation

The Manchester Environmental Laboratory (MEL) will prepare a written quality assurance (QA) review of laboratory QA information that evaluates the validity and usefulness of all metals data. The review will discuss sample holding times, instrument calibration, procedural (method) blanks, matrix spikes, and laboratory control sample (LCS) analyses.

The results of these laboratory QA samples should fall within the guidelines established within the EPA Contract Laboratory Program (CLP). Laboratory QA samples that do not meet CLP requirements will be reanalyzed unless the samples are over the CLP holding time.

Precision

Field

Field QA samples will be collected at a frequency of 10 percent of the total sampling effort. Replicate pairs (sequential samples collected about 15 minutes apart) will constitute 80 percent of the QA samples, 10 percent will be field splits, and 10 percent laboratory splits. Replicate pairs information will be used to provide an estimate of total variability (in-stream,

field and analytical variability). Split samples information will be used to separate analytical variability from sampling variability. Replicate pairs and split information will be reported as percent relative standard deviation (% RSD) (see Summary of Calculations). The Project Leader within AMS will prepare an annual written quality assurance review of field QA information that evaluates the validity and usefulness of all metals data.

Laboratory

Each quarter MEL will analyze, in replicate, either the Standard Reference Material SLRS-2 or low level spikes, preferably one order of magnitude below the chronic criteria (spiking levels = Cd < 0.03 $\mu\text{g/L}$, Cu < 0.3 $\mu\text{g/L}$, Pb < 0.05 $\mu\text{g/L}$, and Hg < 0.001 $\mu\text{g/L}$), and no greater than the chronic criteria. Once established, spiking levels are to remain constant. If analysis of Standard Reference Material is preferred rather than spiked samples for evaluation of precision, spiked samples will still be required to check matrix effects but only at a frequency required by CLP. Information on Standard Reference Material or spikes will be compiled annually to determine the laboratory percent relative standard deviation (% RSD) (see Summary of Calculations).

Laboratory Bias

As described above in the Laboratory Precision section, each quarter MEL will analyze, in replicate, either the Standard Reference Material SLRS-2 or low level spikes preferably one order of magnitude below the chronic criteria (spiking levels = Cd < 0.03 $\mu\text{g/L}$, Cu < 0.3 $\mu\text{g/L}$, Pb < 0.05 $\mu\text{g/L}$, and Hg < 0.001 $\mu\text{g/L}$), but no greater than the chronic criteria. Once established, spiking levels are to remain constant. Information on Standard Reference Material or spikes will be compiled annually to determine the laboratory percent bias (for formulas see Summary of Calculations).

Blanks

Field Blanks (Filter and Bottle)

Filter and bottle blanks will be analyzed with every other field collection to identify if analytes are present in the sample containers or preservative, and if present are a result of sample handling. Bottle blanks will consist of Teflon® sample bottles filled with deionized water at MEL and acidified in the field. Filter blanks will be prepared in the field by filtering deionized water through the Nalgene units and acidifying. All bottle and filter blank results greater than the reporting limits will be reviewed to decide if the sample results are compromised. If the samples are found contaminated in the field the QA data qualifier codes will be increased by one, or more, depending on the degree of contamination (see Data Quality Assurance).

Laboratory Blanks

Laboratory blanks will be analyzed at a frequency of two blanks per analytical batch. All laboratory blank results above the reporting limit will be reviewed by MEL staff to decide if the sample results are compromised. All compromised samples will be reanalyzed. However, if reanalysis is not possible, MEL will assigned a "V" data qualifier code to all data less than 10 time the concentrations determined in the blank. All qualified data will be indicated in the Laboratory QA review.

Analytical Detection Limits

Method Detection Limit Study and Ongoing Verification

Before field collection, MEL will complete the requirements of Section 10.2.2. (Method Detection Limit) of EPA Method 200.8 (Determination of Trace Elements in Water and Waste by Inductively Coupled Plasma - Mass Spectrometry). The MEL will also complete a similar MDL study for low level mercury by cold vapor atomic fluorescence. These MDL studies will be repeated at six month intervals as recommended in EPA Method 200.8. The information from this MDL study will not only be used to determine the current limit of detection, but also to address laboratory percent bias and %RSD at low metal concentrations (for formulas see Summary of Calculations).

Holding Times

Holding times will be the same as those required in the Laboratory Users Manual (Ecology, 1994). All holding time will be six months from the time of collection with the exception of mercury, which will be 28 days.

DATA MANAGEMENT

Laboratory

Metals data will be reported to one significant figure at the MDL, two significant figures at level 10x MDL, and three significant figures at levels greater than 10x MDL. Metals information will be uploaded to the EPA Region 10 Computer System or Manchester's Laboratory Information Management System when operational. A hard copy of the metals data and the laboratory QA evaluation will be forwarded to the Project Leader in the Ambient Monitoring Section. Target turnaround time for metal analysis is 90 days after sample collection.

Ambient Monitoring Section

Data generated to evaluate the Final WY 1994 303(d) List will be stored as an EXCEL spreadsheet and will be provided to the Water Quality Program upon completion of this

project. Data collected to address the Ambient Monitoring related objectives of this project will be stored in the Ambient Monitoring database and PC STORET along with the conventional water quality parameters. Metals information will be uploaded to EPA STORET with the conventional parameters.

DATA QUALITY ASSURANCE

Data from the ambient and 303(d) portion of the metals project will be subject to two levels of verification. "Level one" will pass the data through two checks. The first will check the date of analysis to ensure that holding times are met. The second will evaluate the %RSD for check standards or reference material. Quality codes will be attached to each datum during this "level one" evaluation. They are as follows:

- 1 = %RSD at or near Chronic Criteria is $\leq 5\%$
- 2 = %RSD at or near Chronic Criteria is $\leq 10\%$
- 3 = %RSD at or near Chronic Criteria is $\leq 20\%$
- 4 = %RSD at a factor of ten above Chronic Criteria is $\leq 10\%$
- 5 = %RSD at a factor of ten above Chronic Criteria is $\leq 20\%$ or % RSD at or near Chronic Criteria is $> 20\%$
- 6 = %RSD at a factor of ten above Chronic Criteria $> 20\%$
- 7 = Not assigned
- 8 = Not assigned
- 9 = Datum is unusable (holding time not met)

The "level two" QA check consists of a manual review of the remaining QA information and re-coding the quality code. "Level two" QA checks are as follows:

- 1 = Field blank contamination $>$ twice the laboratory blanks
- 2 = Field replicate or splits %RSD $> 20\%$
- 3 = Laboratory bias of reference materials or check standards $> \pm 10\%$
- 4 = Reference material %RSD $> 20\%$ (if check standards used in initial QA evaluation)

If data quality is further compromised by QA checks in "level two," the data qualifier codes assigned in "level one" will be increased by one for each additional QA problem. Data with final qualifier codes of greater than four will not generally be distributed but available upon special request.

ESTIMATED COST

Metals Screening at Locations Removed from the 1994 303(d) List

	45	Sample sites
	2	Field replicates
	1	Field split
	1	Lab split
	2	Laboratory blanks
	1	Filter blank
	1	Bottle blank
	2	Laboratory spikes
	<u>1</u>	Reference material
	56	per season
x	<u>2</u>	seasons
	112	Total Samples

Laboratory Analysis

112	Ultra Trace dissolved metals \$300	\$33,600
	(Cd, Cu, Ni, Pb, Zn)	
112	Total recoverable \$92	\$10,304
	(As, Cr, Hg)	
	Sample preparation (Hg) @ \$50	\$5,600
	Sample prep total recoverable ICP @ \$15	\$1,680
96	Hardness @ \$16	\$1,536

Sample Collection

106	Filters @ \$30	\$3,180
328	Teflon® bottles @ \$20	\$6,560
212	Preservation acid @ \$10	\$2,120
		\$64,580

Ambient Metals Concentration

10	Locations (see Table 1.)	
1	Field replicate or 1 field split or 1 lab split	
2	Laboratory blanks	
1	Filter blank or 1 bottle blank	
2	Laboratory spikes	
1	Reference material	
<u>17</u>	per sampling effort	
x <u>6</u>	sampling efforts	
102	Total samples	

Laboratory Analysis

102	Ultra trace dissolved metals @ \$300	\$30,600
	(Cd, Cu, Ni, Pb, Zn)	
102	Total recoverable metals @ \$92	\$9,384
	(As, Cr, Hg)	
	Sample preparation (Hg) @ \$50	\$5,100
	Sample preparation total recoverable ICP @ \$15	\$1,530
66	Hardness @ \$16	\$1,056

Sample Collection

72	Filters @ \$30	\$2,160
210	Teflon® bottles @ \$20	\$4,200
144	Preservation acid @ \$10	\$1,440
		<u>\$55,470</u>

Method Detection Limit Study and Ongoing Verification

Method Detection Limit Study (Three Times Per Year)

21	Ultra trace dissolved metals @ \$180	\$3,780
	(Cd, Cu, Pb)	
21	Mercury analysis @ \$ 50	\$1,050
	Sample preparation (Hg) @ \$50	\$1,050
		<u>\$5,880</u>
3	Standard Reference Material (SLRS-2) @ \$200	\$600
		<u>\$ 6,480</u>

GRAND TOTAL \$126,530

GLOSSARY

AMS - Ambient Monitoring Section of the Environmental Investigations and Laboratory Service Program

CLP - Data quality requirements established by the U.S. Environmental Protection Agency Contract Laboratory Program in their most recent Statement of Work (SOW).

Dissolved Metals - The water sample is filtered through a 0.45 μm filter and acidified with concentrated Hydrochloric acid.

ICP or ICAP - Inductively Coupled (Argon) Plasma see Manchester Environmental Laboratory January 1994 page 201.

ICP-MS (Inductively Coupled Plasma - Mass Spectrometry) - method suitable for low level analysis of ambient freshwater (EPA Method 200.8 see Manchester Environmental Laboratory January 1994 page 201).

MDL (Method Detection Limit) - The minimum concentration of an analyte that can be identified, measured and reported with (99% confidence that the analyte concentration is greater than zero. (EPA, 1991) (See Summary of Calculations)

SRM - Standard Reference Material (SLRS-2 is a Canadian riverine water reference material for determination of trace metals, and NIST 1643 C is a reference material for mercury)

TIS - Toxics Investigatin Section of the Environmental Investigations/Laboratory Service Program

Total recoverable - the whole water sample is (no filtration) acidified with nitric acid and digested with a strong acid (HCL).

WY - Wateryear (October 1, 19XX - September 30, 19XX)

305(B) report - A biannual report required as part of the federal Clean Water Act (CWA). This report assesses the states surface waters to insure they meet the fishable, swimmable requirements of Clean Water Act (Ecology, 1992).

303(d) list - a requirement of the 305(B) report to list any water quality segment where the known water quality does not meet applicable water quality standards, and or is not expected to meet applicable water quality standards even after the application of the technology-based controls are in place (Ecology, 1992).

%RSD - Percent Relative Standard Deviation (See Summary of Calculations)

SUMMARY OF CALCULATIONS

$$\% \text{ RSD}^* = (S/X) * 100$$

where

S = Standard deviation (n-1)

X = Mean of laboratory results

$$\% \text{ Bias}^* = \frac{X - T}{T} * 100$$

where

X = Mean of the results of replicate analysis

T = True concentrations

$$\text{MDL}^{**} = t * S$$

where

t = Student's t value for 99% confidence levels and a standard deviation estimate with n-1 degrees of freedom (t=3.14 for 7 replicates)

S = Standard deviation of the 7 replicates.

*From Ecology, 1991.

**From EPA method 200.8.

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APPENDIX A

**Water Segments Listed in the
Preliminary 1994 303(d) List
With Potential Metal Problems**

Appendix A. Water Segments listed in the preliminary 1994 303(d) list with potential metal problems. Bold type face indicates Water Bodies on the final 1994 303(d) list (Ecology, 1994).

Waterbody Segment Number	Waterbody Name	Parameter Exceeding Standards
1) WA-01-1010	Nooksack River	Lead, Cadmium
2) WA-01-1101	Silver Creek	Arsenic
3) WA-01-3110	Whatcom Creek	Metals
4) WA-07-1020	Snohomish River	Copper, Cadmium, Mercury
5) WA-07-1050	Snohomish River	Copper, Cadmium, Mercury
6) WA-08-1010	Juanita Creek	Mercury, Copper, Lead, Zinc
7) WA-08-1012	Forbes Creek	Copper, Lead
8) WA-08-1014	Yarrow Bay Tributary	Copper, Lead
9) WA-08-1016	Fairweather Bay Tributary	Copper, Lead
10) WA-08-1018	Kelsey Creek	Cadmium, Copper, Lead
11) WA-08-1020	Thornton Creek	Cadmium, Copper, Lead, Zinc
12) WA-08-1030	Mcaleer Creek	Mercury, Copper, Lead, Zinc
13) WA-08-1040	Lyon Creek	Cadmium, Copper, Lead, Zinc
14) WA-08-1060	Swamp Creek	Copper, Lead
15) WA-08-1065	North Creek	Cadmium, Copper, Lead
16) WA-08-1070	Sammamish River	Copper, Lead
17) WA-08-1085	Little Bear Creek	Copper, Lead, Zinc
18) WA-08-1095	Bear-Evans Creek	Mercury, Copper, Lead
19) WA-08-1110	Issaquah Creek	Mercury, Copper, Lead
20) WA-08-1115	Tibbetts Creek	Copper, Lead
21) WA-08-1120	Coal Creek	Mercury, Copper, Lead
22) WA-08-1130	May Creek	Copper
23) WA-08-1143	Cedar River @ Logan St Bridge	Copper
24) WA-08-1145	Cedar River @ Maplewood	Copper, Lead, Mercury
25) WA-08-2100	Mercer Slough	Mercury
26) WA-09-1010	Duwamish River	Cadmium, Copper, Lead, Mercury, Zinc
27) WA-09-1015	Springbrook (Mill) Creek	Cadmium, Copper, Lead, Mercury, Zinc
28) WA-09-1020	Green River	Cadmium, Copper, Mercury, Lead
29) WA-09-1022	Hill (Mill) Creek	Copper, Lead
30) WA-09-1026	Soos Creek	Copper, Lead, Nickel, Mercury
31) WA-09-1028	Newaukum Creek	Copper, Lead
32) WA-09-1030	Green River	Mercury, Lead

Appendix A. Continued.

Waterbody Segment Number	Waterbody Name	Parameter Exceeding Standards
33) WA-10-1010	Puyallup River	Copper, Lead, Zinc, Cadmium, Mercury
34) WA-10-1011	Hylebos Creek	Copper, Mercury
35) WA-10-1012	Fife Ditch	Copper, Lead, Zinc, Cadmium
36) WA-10-1015	Wapato Creek	Metals
37) WA-10-1021	Clear Creek	Metals
38) WA-10-1022	Swan Creek	Copper, Mercury
39) WA-10-1025	Clarks Creek	Metals
40) WA-10-1026	Unnamed Creek	Metals
41) WA-10-1027	Diru Creek	Metals
42) WA-11-1010	Nisqually River	Cadmium, Copper, Lead, Mercury
43) WA-13-1010	Deschutes River	Cadmium, Copper, Mercury
44) WA-15-5000	Clear Creek	Metals
45) WA-23-1023	Salzer Creek	Metals
46) WA-25-5010	Longview Ditches	Cyanide, Cadmium, Lead, Zinc
47) WA-28-1023	Cougar Creek	Metals
48) WA-28-1040	Burnt Bridge Creek	Chromium, Lead, Mercury
49) WA-34-1010	Palouse River	Copper, Lead, Mercury
50) WA-37-1030	Sulfer Creek Wasteway	Metals
51) WA-39-1037	Crystal Creek	Metals
52) WA-47-1014	Mitchell Creek	Arsenic
53) WA-47-1020	Railroad Creek	Arsenic
54) WA-47-1030	Stehekin River	Arsenic
55) WA-54-1020	Spokane River	Cadmium, Copper, Lead, Mercury, Zinc
56) WA-55-1010	Little Spokane River	Cyanide, Mercury
57) WA-57-1010	Spokane River	Cadmium, Copper, Lead, Mercury, Zinc
58) WA-CR-1010	Columbia River	Copper, Lead, Zinc, Cadmium, Copper, Chromium, Mercury
59) WA-CR-1020	Columbia River	Copper, Lead, Zinc, Cadmium, Copper, Mercury
60) WA-CR-1030	Columbia River	Lead, Mercury, Copper
61) WA-CR-1060	FDR Lake	Cadmium, Copper, Lead, Mercury, Zinc

APPENDIX B
Supporting Information

Appendix B. Supporting Information.

Ecology's Previous Ambient Metals Monitoring

The freshwater ambient monitoring unit has collected metals information (Total Recoverable Cd, Cu, Pb, Cr, Zn and Total Hg) from 1987 to 1991 at 13 stations listed in Table 1. Metals information was also collected before 1987, however, due to limitations of the data this information was not enter into our database or uploaded to STORET. The most significant limitation of the older data set was the lack of QA information. Metals information from 1987 to 1991 was within acceptable QA range and was entered into our data management system and STORET. AMS eliminated metals from it's parameter list at the end of Wateryear 1991 (September 30, 1991) at all stations except the Columbia River, at Northport and select floating stations where metals information was deemed critical.

Table 1. Freshwater ambient monitoring stations with metals information (1987-1992).

Station ID	Segment Number	303(d) Listing	Station Name
1) 01A050	WA-01-1010	Y	Nooksack River
2) 07A090	WA-07-1020	Y	Snohomish River
3) 09A060	WA-09-1010	Y	Duwamish River
4) 09E070	WA-09-1015	Y	Springbrook (Mill Creek)
5) 09E090	WA-09-1015	Y	Springbrook (Mill Creek)
6) 09A090	WA-09-1020	Y	Green River
7) 11A070	WA-11-1010	Y	Nisqually River
8) 13A060	WA-13-1010	Y	Deschutes River
9) 34A070	WA-34-1010	Y	Palouse River
10) 54A120	WA-54-1020	Y	Spokane River
11) 55B070	WA-55-1010	Y	Little Spokane River
12) 57A190	WA-57-1010	Y	Spokane River
13) 36A070	WA-CR-1030	Y	Columbia River

Applying the New Metals Criteria to Ecology's Historic Ambient Metals Information

Problems can arise when comparing the Washington State Chronic Water Quality Criteria (Chronic Criteria) to non-qualified low level metals data. Table 2 lists the current 1992 Water Quality Criteria for Washington State for select metals (WAC 173-201A). Table 3 lists the current detection limits for the specific metals and the corresponding water quality criteria for metals based on a hardness of 25. Chronic criteria for lead and mercury do not consider the limitations of the current State and EPA NPDES approved analytical methods. Thus the resulting criteria are less than the detection limits of the accepted analytical method.

Table 2. Washington State Water Quality Criteria for Select Metals.

Metal	Criteria
Arsenic (As)	Acute = 360 $\mu\text{g/L}$
	Chronic = 190 $\mu\text{g/L}$
Cadmium (Cd)	Acute = $\leq (0.865)(e^{1.128[(\ln(\text{hardness})]-3.828)})$
	Chronic = $\leq (0.865)(e^{0.7852[(\ln(\text{hardness})]-3.490)})$
Chromium (Cr) (Hex)	Acute = 16.0 $\mu\text{g/L}$
	Chronic = 11.0 $\mu\text{g/L}$
Chromium (Cr) (Tri)	Acute = $\leq (e^{0.8190[(\ln(\text{hardness})]+3.688)})$
	Chronic = $\leq (e^{0.8545[(\ln(\text{hardness})]+1.561)})$
Copper (Cu)	Acute = $\leq (0.862)(e^{0.9422[(\ln(\text{hardness})]-1.464)})$
	Chronic = $\leq (0.862)(e^{0.8545[(\ln(\text{hardness})]-1.465)})$
Lead (Pb)	Acute = $\leq (0.687)(e^{1.237[(\ln(\text{hardness})]-1.460)})$
	Chronic = $\leq (0.687)(e^{1.237[(\ln(\text{hardness})]-4.705)})$
Mercury (Hg)	Acute = 2.4 $\mu\text{g/L}$
	Chronic = 0.012 $\mu\text{g/L}$
Nickel (Ni)	Acute = $\leq (0.95)(e^{0.8460[(\ln(\text{hardness})]+3.3612)})$
	Chronic = $\leq (0.95)(e^{0.8460[(\ln(\text{hardness})]+1.1645)})$
Zinc (Zn)	Acute = $\leq (0.891)(e^{0.8473[(\ln(\text{hardness})]+0.8604)})$
	Chronic = $\leq (0.891)(e^{0.8473[(\ln(\text{hardness})]+0.7614)})$

Table 3. Manchester Analytical Laboratory Current Detection limits and corresponding chronic criteria for select metals (based on hardness of 25 mg/L for Cd, Cu, Pb and Zn).

Metal	Detection Limit	Chronic Criteria
Cadmium	0.1 (AA)	0.330
Copper	1.0 (AA)	3.12
Lead	1.0 (AA)	0.374
Mercury	0.05 (CV)	0.012
Zinc	4.0 (AA)	29.12

For example, Manchester Environmental Laboratory historically has a detection limit of 0.05 $\mu\text{g/L}$ for mercury and the chronic criterion is 0.012 $\mu\text{g/L}$. If the laboratory reports a value of 0.05 $\mu\text{g/L}$, this value would be a violation of chronic criteria. Laboratory precision is ideally 95 percent at the detection limits but is often much less and false positive violations may occur. Another problem with detection limits above the chronic criteria is that violations between the detection limit and the chronic criteria will be missed. Using mercury again as an example, with the historical detection limit of 0.05 $\mu\text{g/L}$ concentrations $>0.012 \mu\text{g/L}$ and <0.05 that are be violations of chronic criteria would be missed.

APPENDIX C

Preliminary Methods Study

PRELIMINARY METHOD STUDY

Objectives

The objectives of this preliminary method study were as follows:

- 1) to compare sampling techniques of the Toxics Investigation Section (TIS) to those of the Ambient Monitoring Section (AMS); and
- 2) to determine the total variability within ambient metal samples.

Study Design

From November 1992 to May of 1993, TIS and AMS collected bi-monthly water samples at three locations. These three locations were the Puyallup River at Meridian St. Bridge, Green River near Kanaskat, and Green River at Tukwila. These sampling efforts were identical with the exception that TIS collected water samples by wading or with the aid of a long-handled dipper, and the AMS samples were collected with the aid of a stainless steel sampler lowered by rope from a bridge.

The following is an overview of the sample collection scheme of the method comparison study:

- 12 Total Replicate Pairs (here after called co-located) between TIS and AMS
- 2 Additional Replicate Pairs (here after called Sequential) TIS (subset of 12)
- 2 Additional Replicate Pairs (Sequential) AMS (Subset of 12)
- 2 Additional Split Samples (Field) TIS
- 2 TIS Method Blanks
- 2 AMS Method Blanks
- 2 TIS Bottle Blanks
- 2 AMS Bottle Blanks
- 2 Standard Reference Materials (SLRS-2 and NIST 1643c)

Methods (see Ambient Metals Project Proposals Methods)

Field processing and laboratory analysis were identical between both sampling efforts. Manchester Laboratory analyzed for total recoverable metals and the Battelle Laboratory analyzed for total and dissolved metals.

Results of Replicate Pairs

Table 1 provides the paired samples results. It should be noted that 253 of 336 or over 75% of the metals results were qualified by the Laboratories. Qualified data was not corrected

Table 1. Results of preliminary method study.

Table 1. Results of Preliminary Method Study Paired Samples.

Date	Sample Location	Analytical Method	Metals Concentration in ug/L										Hard
			AMS Cd	TCGWIS Cd	AMS Cu	TCGWIS Cu	AMS Hg	TCGWIS Hg	AMS Pb	TCGWIS Pb	AMS Zn	TCGWIS Zn	
23-Nov-92	Green	Total	0.008 B	0.006 B	1.03	0.696	0.00203 J		0.163 B	0.122 B	1.8 B	1.65 B	
25-Jan-93		Total	0.054	0.051	11	17	0.11421 J		1.86	1.96	8.95 B	7.49 B	
29-Mar-93		Total	0.01 B	0.002 B	0.31	0.26	0.00181 B		0.09 B	0.04 B	1.76 B	1.76 B	
24-May-93		Total	0.003 J	0.004 J	0.59	0.29	0.00144 J		0.064 J	0.075 J	0.71 J	0.38 J	
23-Nov-92	Green	Dissolved	0.041	0.005 B	1.1	0.431	NA		0.092 B	0.031 B	1.42 B	1.2 B	
25-Jan-93		Dissolved	0.004 B	0.006 B	0.477 B	0.405	NA		0.085 B	0.076 B	1.63 B	0.9 B	
29-Mar-93		Dissolved	0.004 B	0.002 B	0.25	0.21	NA		0.04 B	0.04 B	1.99 B	1.03 B	
24-May-93		Dissolved	0.002 J	0.003 J	0.31	0.28	NA		0.053 J	0.117 J	0.34 J	1.01 J	
23-Nov-92	Green	Total Rec	0.1 U	0.1 U	4.6 P	1 U	0.701	0.05 U	1 U	1 U	26 J	13 J	39.6
25-Jan-93		Total Rec	0.1 U	0.1 U	9.2 P	8.3 P	0.054 P	0.05 U	2 P	1.9 P	15 P	13 J	34.8
29-Mar-93		Total Rec	0.1 U	0.1 U	1 U	1 U	0.05 U	0.05 U	1 U	1 U	4 U	4 U	13.8
24-May-93		Total Rec	0.1 U	0.1 U	1 U	1 U	0.05 U	0.05 U	1 U	1 U	4 U	4 U	14.6
23-Nov-92	Duwamish	Total	0.036	0.017 B	2.7	1.75	0.00159 J		0.622	0.429	6.3	4.05	
25-Jan-93		Total	0.035	0.041	3.42	3.8	0.00906 J		1.66	1.96	8.71	9.52 B	
29-Mar-93		Total	0.008 B	0.008 B	1.03	0.99	0.00443 B		0.26 B	0.23 B	3.09 B	2.43 B	
24-May-93		Total	0.018 B	0.005 J	1.85	0.69	0.0023 B		0.287 J	0.128 J	2.94 J	0.88 J	
23-Nov-92	Duwamish	Dissolved	0.009 B	0.007 B	1.18	1.01	NA		0.082 B	0.143 B	1.8 B	2.32	
25-Jan-93		Dissolved	0.018 B	0.021	1.98	1.98	NA		0.294	0.303	7.97 B	5.78 B	
29-Mar-93		Dissolved	0.005 B	0.005 B	0.55	0.65	NA		0.08 B	0.11 B	1.32 B	1.84 B	
24-May-93		Dissolved	0.003 J	0.004 J	0.47	0.54	NA		0.075 J	0.064 J	0.76 J	0.5 J	
23-Nov-92	Duwamish	Total Rec	0.11 P	0.1 U	2.2 P	1.7 P	0.756	0.05 U	1 U	1 U	46.3 B	41 B	23.3
25-Jan-93		Total Rec	0.1 U	0.1 U	2.8 P	2.2 P	0.063 P	0.05 U	2.3 P	2.2 P	10 P	8.8 P	35.9
29-Mar-93		Total Rec	0.1 U	0.1 U	1 U	1 U	0.05 U	0.05 U	1 U	1 U	4 U	4 U	23.8
24-May-93		Total Rec	0.1 U	0.1 U	1 U	1 U	0.05 U	0.05 U	1 U	1 U	4 U	4 U	33.9

Table 1. Continued.

Date	Sample Location	Analytical Method	Metals Concentration in ug/L										Hard
			AMS Cd	TCGWIS Cd	AMS Cu	TCGWIS Cu	AMS Hg	TCGWIS Hg	AMS Pb	TCGWIS Pb	AMS Zn	TCGWIS Zn	
23-Nov-92	Puyallup	Total	0.023 B	0.014 B	6.07	3.8	0.00210 J		0.684	0.51	6.67	8.47	
25-Jan-93		Total	0.133	0.091	45.7	40.3	0.02830 J		4.4	4.5	44.6	38.5	
29-Mar-93		Total	0.006 B	0.005 B	1.18	1.13	0.00310 B		0.2 B	0.19 B	2.06 B	2.21 B	
24-May-93		Total	0.015 B	0.006 J	2.22	2.19	0.00302 B		0.287 J	0.245 J	2.18 J	1.43 J	
23-Nov-92	Puyallup	Dissolved	0.144	0.022 B	2.02	1.6	NA		0.235	0.082 B	145	1.42 B	
25-Jan-93		Dissolved	0.019 B	0.01 B	2.39	1.83	NA		0.095 B	0.137 B	3.99 B	1.63 B	
29-Mar-93		Dissolved	0.005 B	0.007 B	0.79	0.81	NA		0.09 B	0.13 B	1.62 B	1.03 B	
24-May-93		Dissolved	0.003 J	0.003 J	1.41	1.04	NA		0.213 J	0.362 B	0.97 J	0.63 J	
23-Nov-92	Puyallup	Total Rec	0.1 U	0.1 U	4 P	3.3 P	0.05 U	0.05 U	1 U	1.2 P	35 J	34 J	24.3
25-Jan-93		Total Rec	0.13 P	0.12 P	33.9	32.4	0.098 P	0.05 U	5.9 P	6.3 P	34 P	33 P	44.1
29-Mar-93		Total Rec	0.1 U	0.1 U	1.1 P	1 U	0.050 U	0.05 U	1 U	1 U	4 U	4 U	24.4
24-May-93		Total Rec	0.1 U	0.1 U	2.1 P	1.4 P	0.050 U	0.05 U	1 U	1 U	4 U	4 U	21.5

B = Detected in Blank

J = Estimate

P = Below Quantitation Limit

and used directly as reported in all calculations unless otherwise noted. Table 2 provides the percent relative standard deviation (%RSD) based on pooled standard deviation of duplicate results. Also included in Table 2 is the precision for the total recoverable method, and the calculated precision for Battelle spikes and TIS sample split.

The %RSD between the co-located paired samples were generally good for most metals except dissolved cadmium, total mercury, dissolved lead, and total recoverable zinc. Review of the data for the dissolved lead and total recoverable zinc show blank problems. With the qualified data removed the %RSD for dissolved lead dropped to 14.9% and total recoverable zinc dropped to 11.76%. The elevated %RSD for mercury and dissolved cadmium are the result of two elevated sample collected during the first sampling effort in November of 1992. With both pairs removed the %RSD dropped to 39.84% and 0.0% for dissolved cadmium and mercury, respectively. For mercury, one complicating factor is that the sample expressing blank contamination was collected as a sequential sample and the result was below the detection limit (initial sample = 0.701 $\mu\text{g/L}$, sequential sample = 0.05U $\mu\text{g/L}$).

Wilcoxon Signed Rank Test

Figures 1 to 6 provide a graphic comparison of the paired samples and the results of the Wilcoxon Signed Rank Test (Non-parametric equivalent of the Paired T Test). As these figures show the only significant difference greater or equal to 90% was found in the following metal fractions;

- 1) Total Recoverable Copper at 99% significant
- 2) Dissolved Copper at 90% significant
- 3) Total Cadmium at 95% significant
- 4) Total Recoverable Zinc at 95% significant

Comparison of Blank Results

TIS and AMS transport blank and filter blank results are presented in Table 3. Blank results were good with most concentrations qualified and near the method detection limits. The only exceptions were three copper concentrations found in both TIS and AMS blanks. November TIS blanks showed a filter blank concentration of 1.81 $\mu\text{g/L}$ and a transport (bottle) blank of 0.076 B $\mu\text{g/L}$. This large difference between blanks could show the possibility of field contamination during the filtration process. However, the possibility of field contamination is not reflected in the data set as the highest sample concentration is at or below this blank concentration. The AMS blank for May shows both bottle and filter blank contamination. More than half the contamination detected in the filter blank (0.1 $\mu\text{g/L}$), however, could be attributed to the bottle blank (0.06 $\mu\text{g/L}$). With the filter blank corrected for the bottle blank contamination the residual is similar to the levels found in the remaining blanks.

Table 2. Comparative Relative Standard Deviation of replicate samples from the TIS and AMS metals screening study.

Source	Method	Number	%RSD	Mean	Precision
<u>Cadmium</u>					
Co-located	TR	12	2.8	0.10	16% @ 2.5*
Toxics Seq.	TR	2	0.0	0.1	
Ambient Seq.	TR	2	4.88	0.103	
Co-located	T	12	47.47	0.04	7% @ 0.01**
Toxics Seq.	T	2	4.08	0.012	8% @ 0.01***
Ambient Seq.	T	2	43.40	0.019	
Co-located	D	12	177.6	0.02	7% @ 0.01**
Toxics Seq.	D	2	40	0.005	8% @ 0.006***
Ambient Seq.	D	4	18.78	0.009	
<u>Copper</u>					
Co-located	TR	12	17.3	4.97	40% @ 11.0*
Toxics Seq.	TR	2	0.0	1.7	
Ambient Seq.	TR	2	9.84	1.53	
Co-located	T	12	27.89	6.25	24% @ 0.05**
Toxics Seq.	T	2	3.66	1.37	1.8 @ 1.37***
Ambient Seq.	T	2	7.68	1.84	
Co-located	D	12	21.93	0.99	24% @ 0.05**
Toxics Seq.	D	2	17.41	0.57	8.9% @ 0.78***
Ambient Seq.	D	4	7.89	1.03	
<u>Mercury (Manchester)</u>					
Co-located		12	208.45	0.09	NA
Toxics Seq.		NA			
Ambient Seq.		2	155.85	0.227	
<u>Mercury (Battelle)</u>					
Ambient Seq.		2	41.45	0.0026	7.5% @ 0.0002**

Table 2. Continued.

Source	Method	Number	%RSD	Mean	Precision
<u>Lead</u>					
Co-located	TR	12	5.92	1.62	32% @ 24.0*
Toxics Seq.	TR	2	90.41	1.83	
Ambient Seq.	TR	2	0.0	1.0	
Co-located	T	12	10.70	0.84	14% @ 0.1**
Toxics Seq.	T	2	13.26	0.312	4.2% @ 0.34****
Ambient Seq.	T	2	12.06	0.443	
Co-located	D	12	40.17	0.13	14% @ 0.1**
Toxics Seq.	D	2	23.36	0.111	11.5% @ 0.13****
Ambient Seq.	D	4	167.88	0.336	
<u>Zinc</u>					
Co-located	TR	12	5.92	1.62	45% @ 16.0*
Toxics Seq.	TR	2	19.51	20.5	
Ambient Seq.	TR	2	50.94	34.08	
Co-located	T	12	10.70	0.84	45% @ 0.22**
Toxics Seq.	T	2	6.90	3.40	1.64% @ 3.24****
Ambient Seq.	T	2	8.74	4.635	
Co-located	D	12	40.17	0.13	45% @ 0.22**
Toxics Seq.	D	2	125.49	5.02	10.4% @ 1.94****
Ambient Seq.	D	4	48.67	2.62	

Toxics Seq. - Toxics sequential samples
 Ambient Seq. - Ambient sequential samples

TR - Total Recoverable

T - Total

D - Dissolved

Rep - Replicate

* - Method precision established in EPA Methods for Chemical Analysis of Water and Waste, EPA-600/4-79-020 (rev, March, 1983)

** - Spike precision established in Federal Register MDL Study (Crecelius, July 21, 1992, letter to B. Kammin).

*** - Precision calculated from blind split samples

NA - Not Analyzed

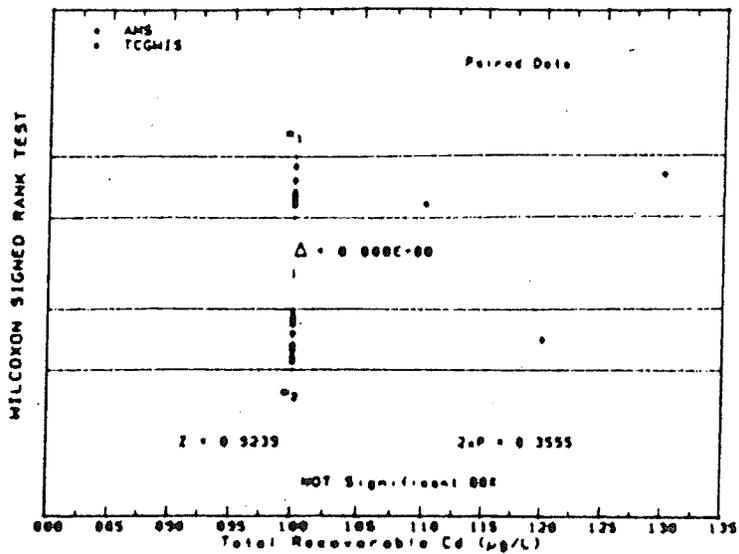
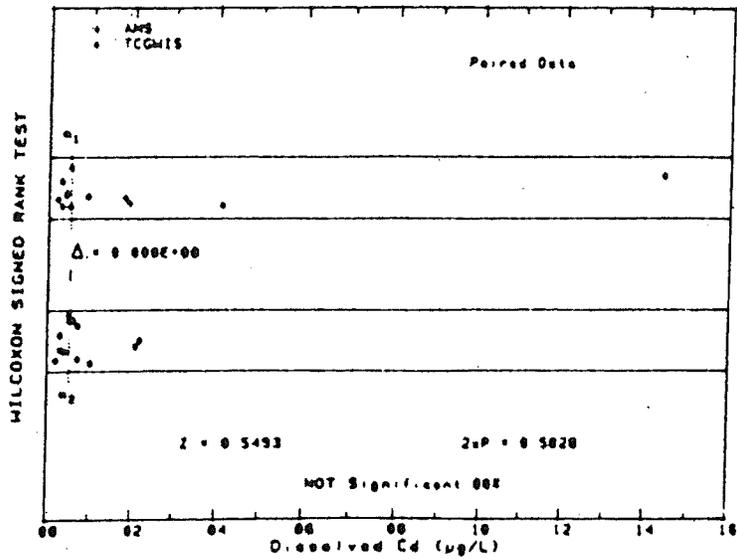
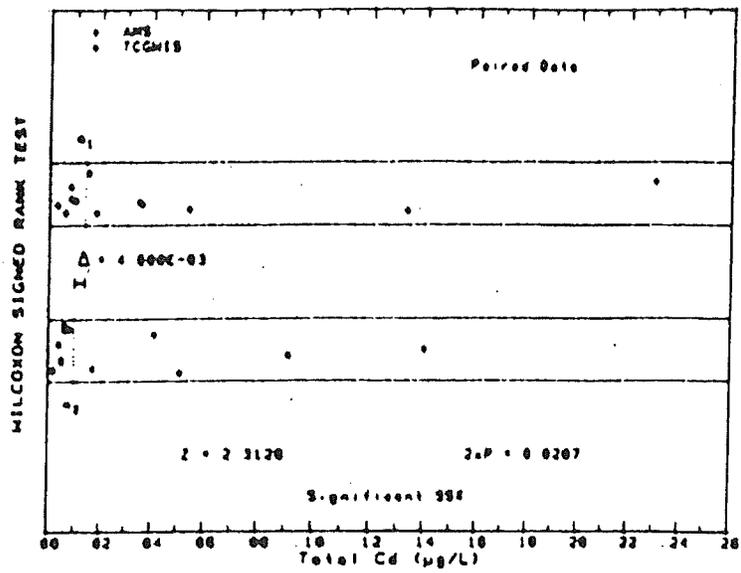


Figure 1. Wilcoxon Signed Rank Test on paired AMS and TCGWIS cadmium results.

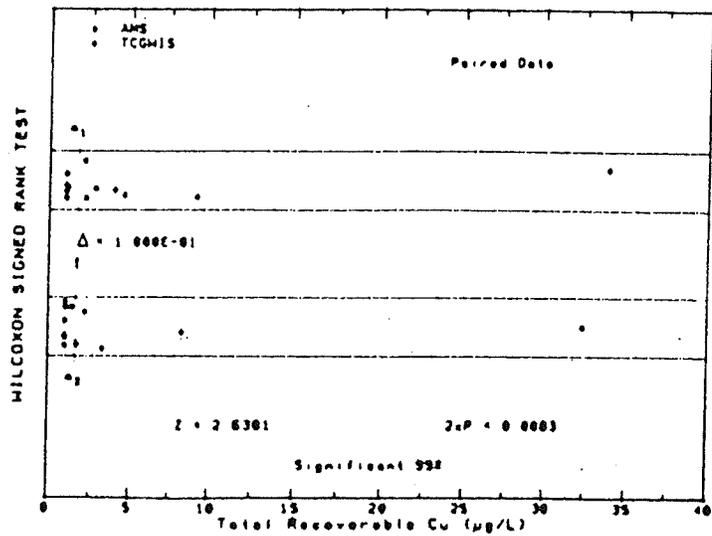
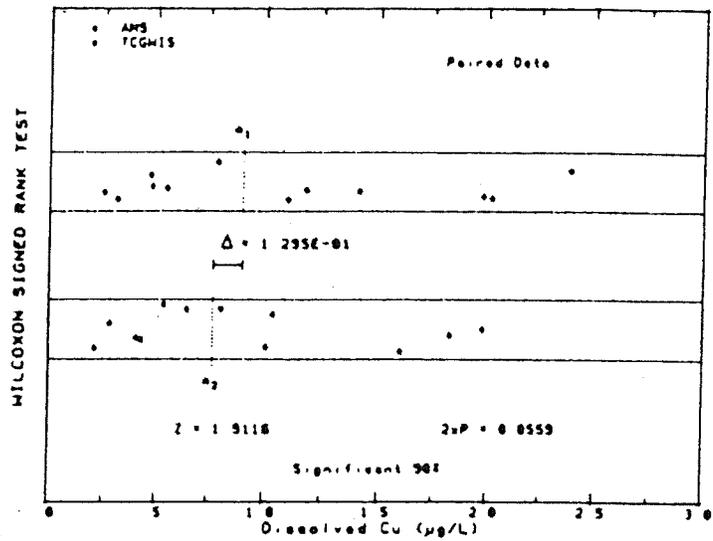
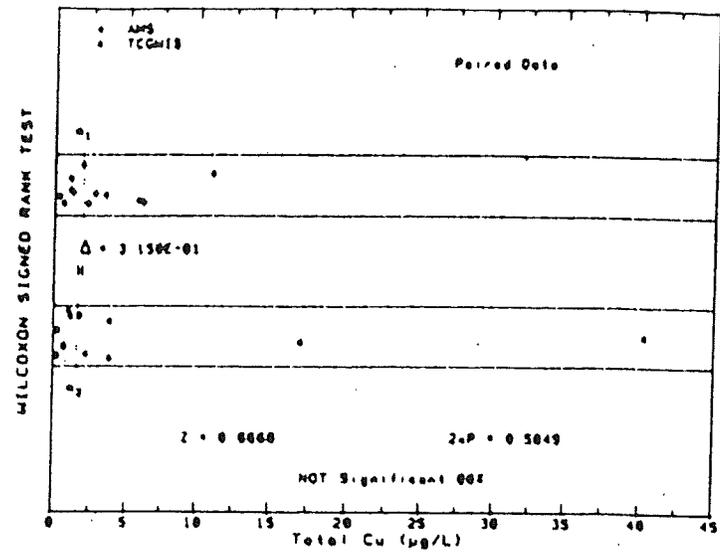


Figure 2. Wilcoxon Signed Rank Test on paired AMS and TCGWIS copper results.

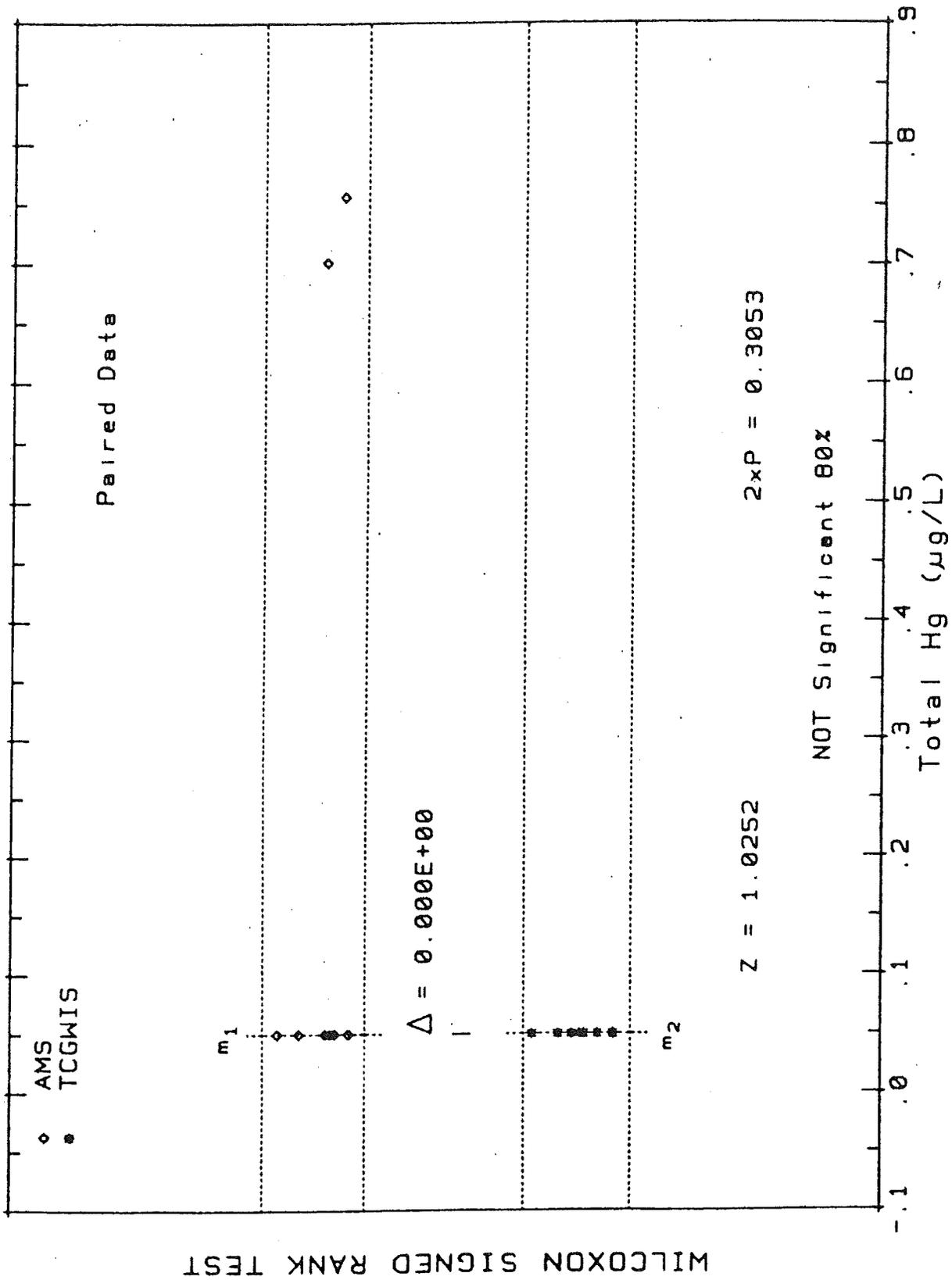


Figure 3. Wilcoxon Signed Rank Test on paired AMS and TCGWIS mercury results.

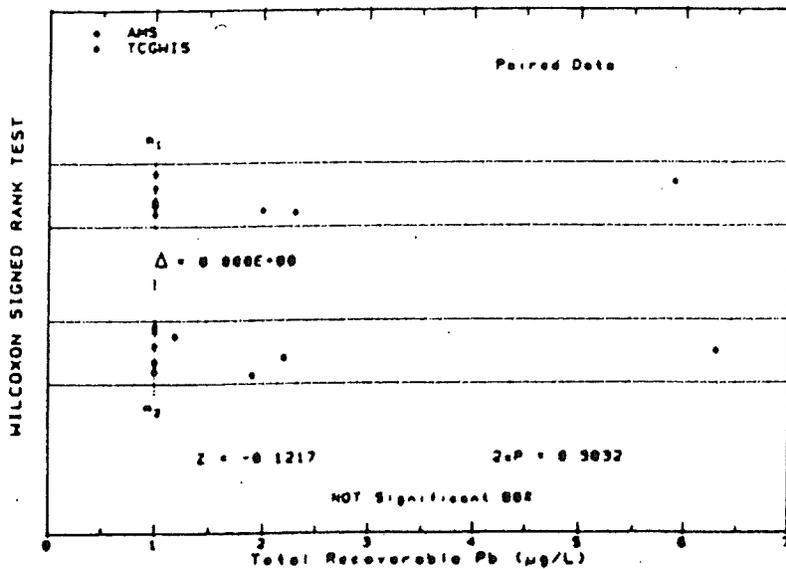
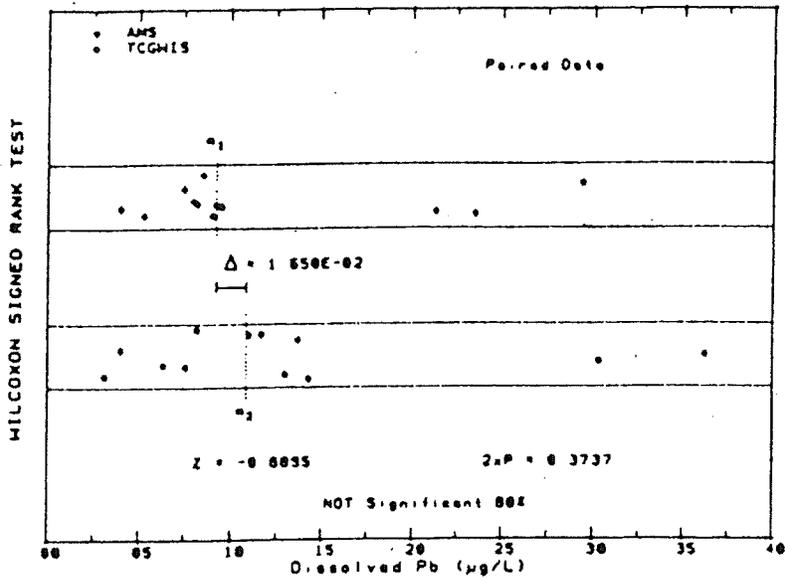
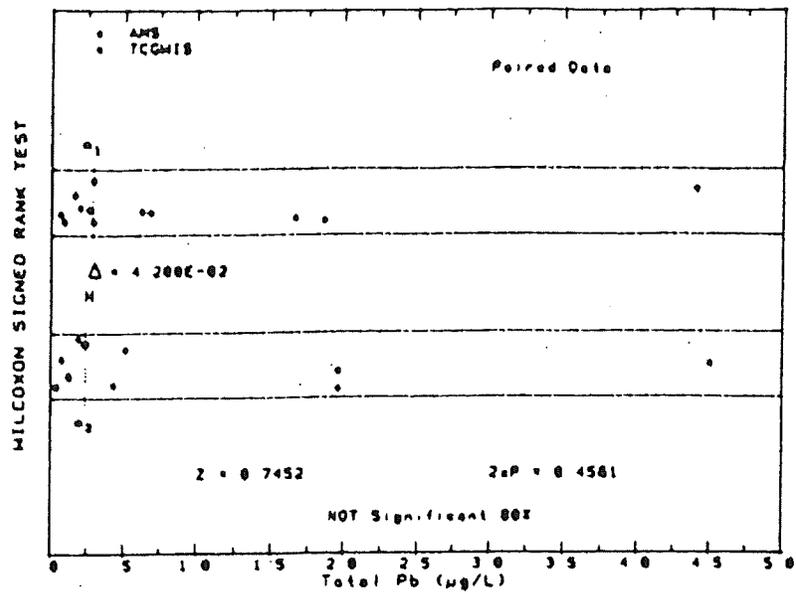


Figure 4. Wilcoxon Signed Rank Test on paired AMS and TCGWIS lead results.

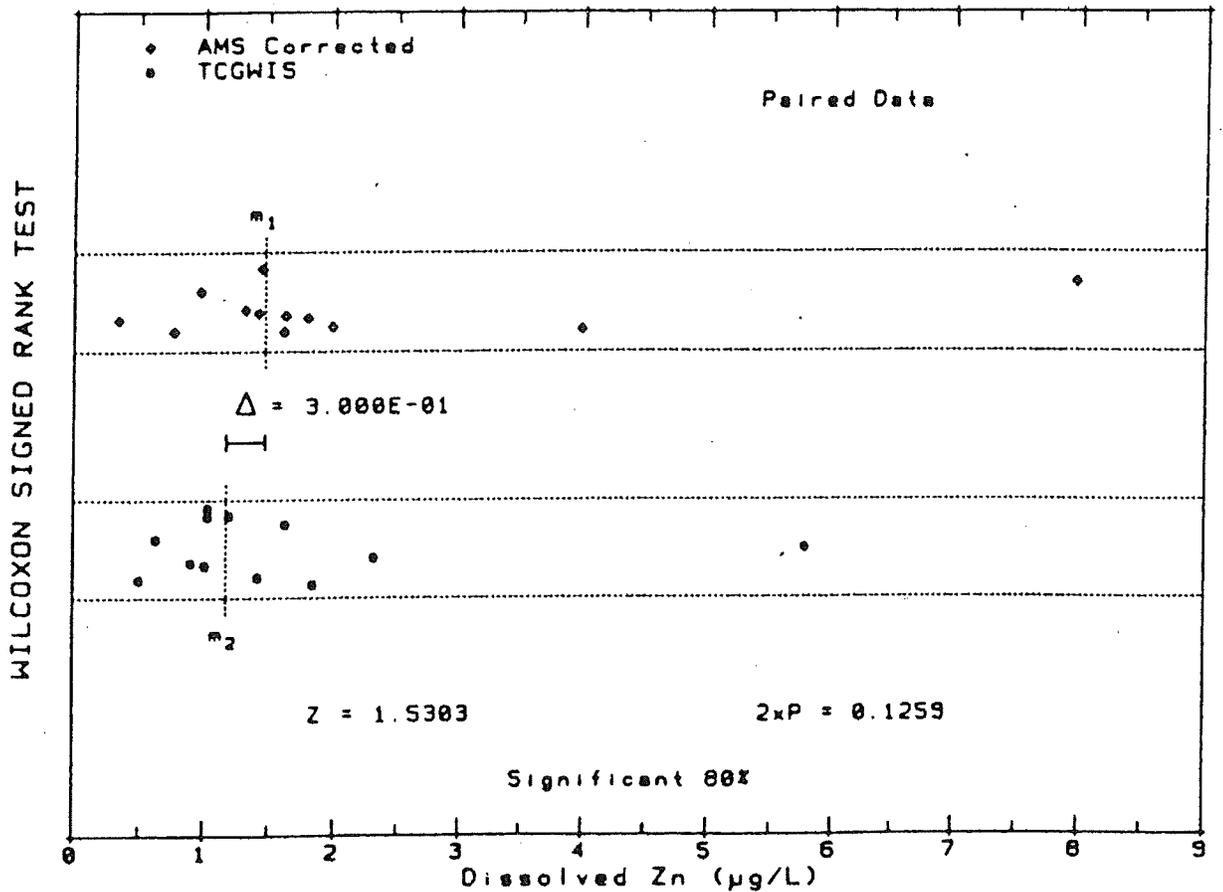
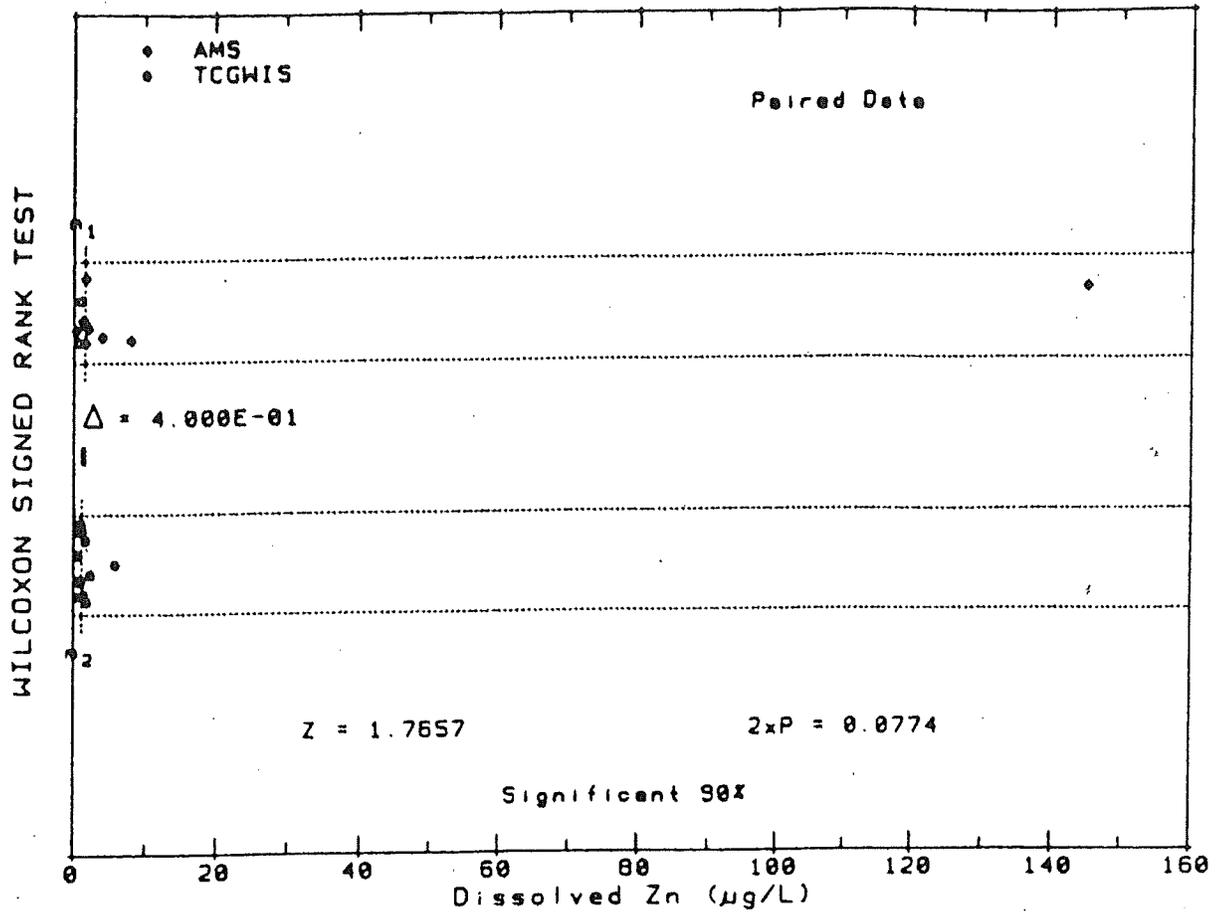


Figure 5. Wilcoxon Signed Rank Test on paired AMS and TCGWIS zinc results.

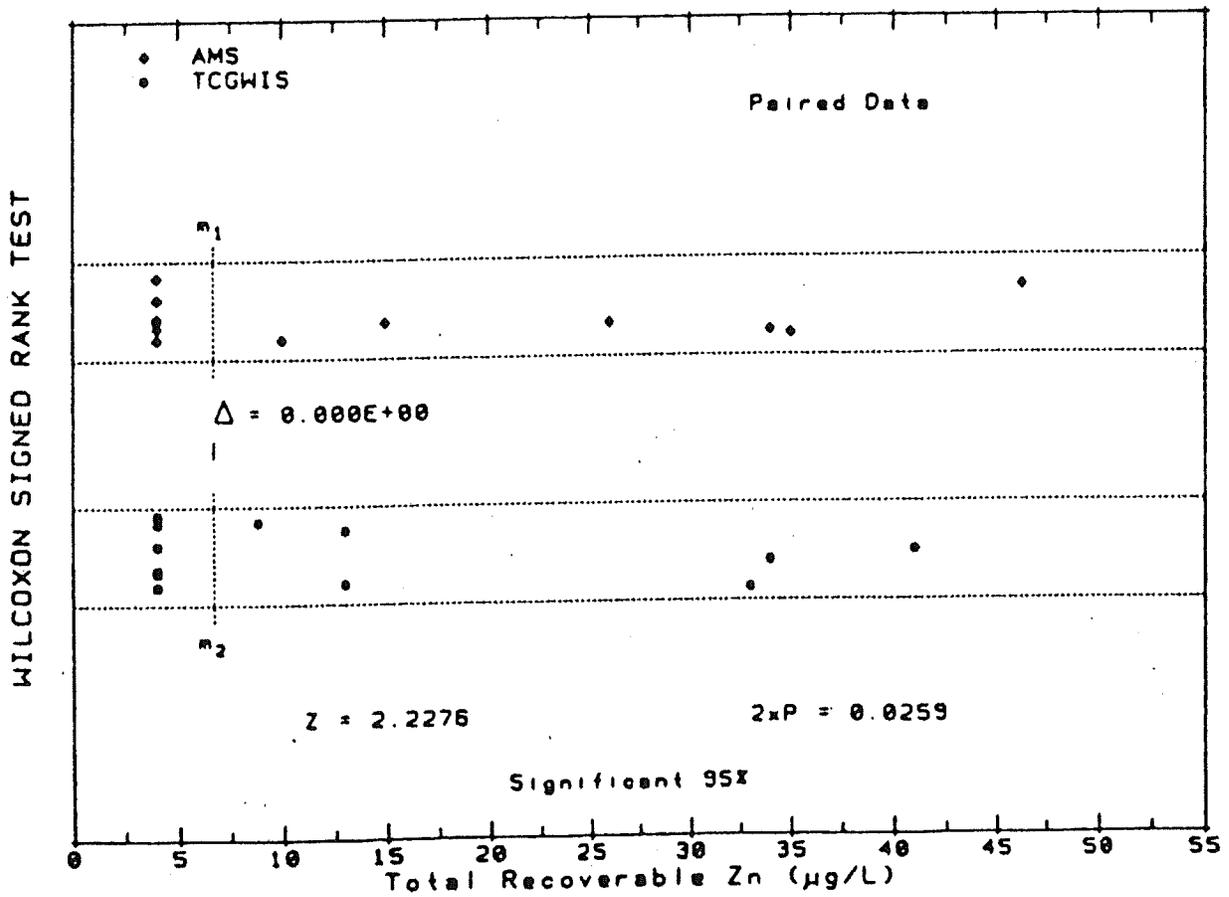
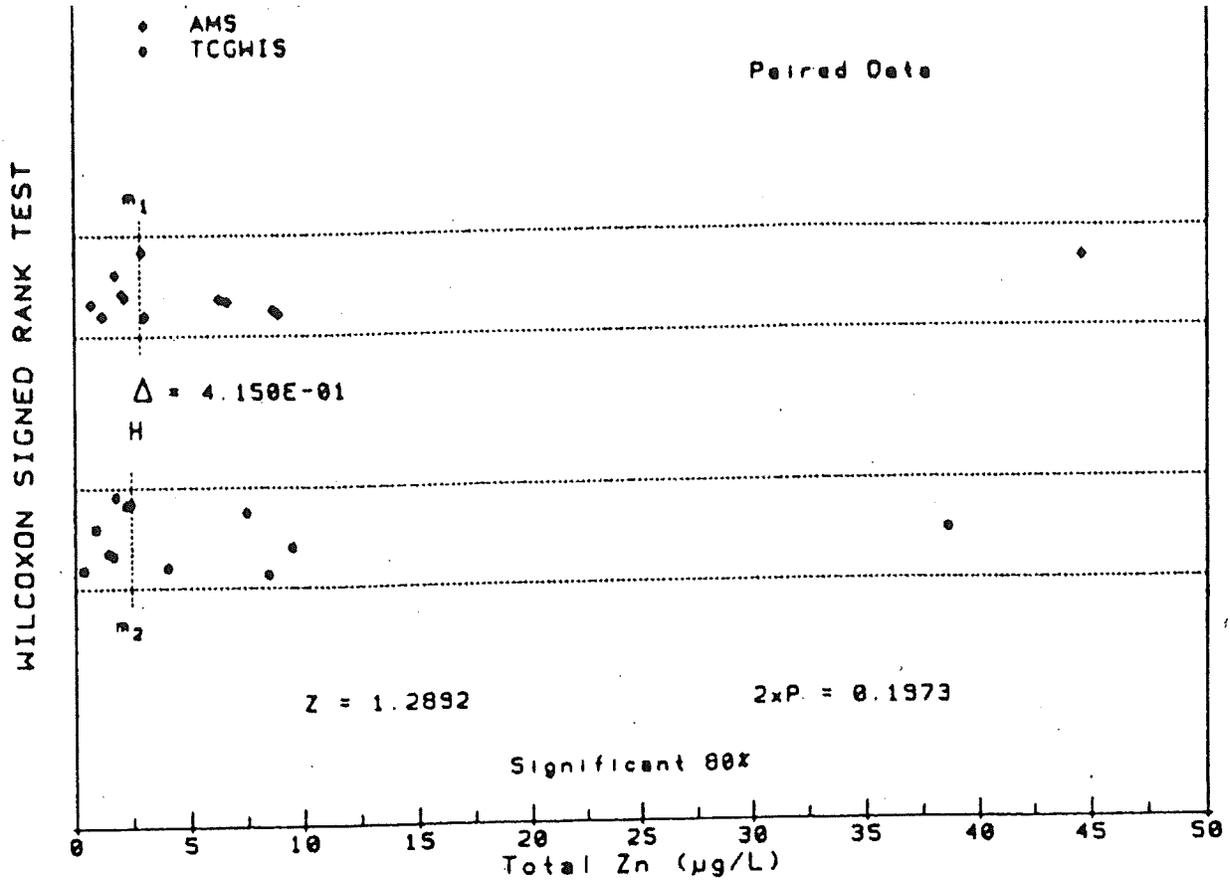


Figure 6. Wilcoxon Signed Rank Test on paired AMS and TCGWIS zinc results.

Table 3. Bottle and filter blank results for the TIS and AMS method comparison study.

Month	Blank Type	Cd	Cu	Pb	Zn
AMS Blanks					
Jan	Bottle	0.022B	0.038B	0.047B	0.9B
Jan	Filter	0.005B	0.084B	0.085B	0.73B
May	Bottle	0.001UJ	0.06	0.032UJ	0.46J
May	Filter	0.005J	0.1	0.053J	1.3J
TIS Blanks					
Nov	Bottle	0.001B	0.076B	0.031B	0.9B
Nov	Filter	0.001B	1.81	0.031B	1.2B
Mar	Bottle	0.001J	0.0016J	0.04J	1.3B
Mar	Filter	0.001J	0.0016J	0.03J	1.8B

B = Detected In Blank

U = Less than

J = Estimated value

Laboratory Precision and Accuracy

Both the internal spikes and field split samples showed good precision as reflected by the %RSD presented in Table 2. The results of the Standard Reference Materials (SRM), however, were not as good. The SRM were submitted blind to the laboratories and the results are presented in Table 4. SRM results for the Battelle Laboratory (analyzed for total and dissolved metals) were high for both the low-level SLRS-2 and high-level NIST 1643c reference materials. SLRS-2 concentrations were above Ecology's Manchester Laboratory (analyzed the total recoverable metals) detection limits for all but copper and therefore of limited usefulness. Manchester total recoverable copper results was below the certified concentration present in SLRS-2.

Conclusion

The results of the methods comparison study suggests AMS methods and sampler are adequate for the collection of low level metal information. However, there was a statistical difference between the paired samples collected by the AMS and TIS for total recoverable and dissolved copper, total cadmium and total recoverable zinc. The limited number of sample pairs, the poor performance on Standard Reference Materials, the high number of qualified data and blank contamination make it difficult to determine if the samples are truly different or are a result of poor laboratory performance. Blank contamination present in the bottles and filters compromised the dissolved copper results (see Table 3). Poor performance on the Standard Reference Material limits the usefulness of the three remaining metal

Table 4. Analysis of Standard Reference Materials Submitted Blind to the Laboratories.
(Battelle (total (T) and Manchester (Total Recoverable (TR)))

Type of SRM	Month	TR-Cd	T-Cd	TR-Cu	T-Cu	TR-Pb	T-Pb	TR-Zn	T-Zn
SLRS-2									
	Nov	NA	0.06	NA	3.42	NA	0.235	NA	4.95
	Jan	NA	0.038	NA	3.37	NA	0.18	NA	4.8B
	March	0.1U	0.032	2.2P	2.51	1U	0.15B	4U	3.38B
	May	0.1U	0.033B	2.3P	2.74	1U	0.149J	4U	2.52J
	Mean		0.04075		3.01		0.1785		3.9125
	Std Dev		0.01134		0.39		0.0349		1.0107
	95% CI		0.0361		1.25		0.111		3.22
Lab Values			0.041 ± 0.0361		3.01 ± 1.25		0.179 ± 0.111		3.9125 ± 3.22
Certified Value			0.028 ± 0.004		2.76 ± 0.17		0.129 ± 0.011		3.33 ± 0.15
NIST 1643c									
	Nov	12.6	13.4	21	26	36.6	37.3	119B	136
	Jan	13	12.6	19	25.9	38.2	36.6	64	134
	March	13.2	1.7	18.7	23.7	37	34.7	72.8	86.7
	May	12.8	51.6R	18.1	21.8	39.6	35.7	69.7	100
	Mean	12.9	22.33	19.2	24.35	37.85	36.08	81.4	114.2
	Std Dev	0.22	16.9	1.08	1.74	1.17	0.98	22.0	21.4
	95% CI	0.71	53.8	3.46	5.52	3.72	3.1	69.9	68
Lab Values		12.9 ± 0.71	22.3 ± 53.8	19.2 ± 3.5	24.4 ± 5.5	37.8 ± 3.7	36.1 ± 3.1	81.4 ± 70	114.2 ± 68
Certified Values		12.2 \pm 1.0		22.3 \pm 2.8		35.3 \pm 0.9		73.9 \pm 0.9	

fractions. This study does, however, show there are still limitations with the analytical methods that need to be overcome. Detection limits need to be lower and the precision at these low levels needs to be improved. Following this method comparison study the Manchester Laboratory has improved its low level metal capabilities. Table 5 shows blank results for the total recoverable method originally reported in a memo from Bill Kammin to Greg Pelletier dated November 29, 1993. These results suggest the Manchester instruments can work in the range AMS expects to find in the rivers and streams to be monitored. However, before starting field sampling it would be helpful to assess laboratory precision with low level spike results. Ideally, spiking levels should be at least one order of magnitude below the chronic criteria (spiking levels = Cd < 0.03 µg/L, Cu < 0.3 µg/L, Pb < 0.04, and Hg < 0.001 µg/L). Review of Manchester's blank results suggest the current instrument detection limits (Table 5) are adequate for most metals except lead. However, if spiking at these low levels is not practical, then Canadian River Water Standard Reference Material SLRS-2 should be substituted.

Table 5. Total recoverable blank results for the Manchester Environmental Laboratory (µg/L).

Blank	Cu	Pb	Cd	Zn
Prep	-0.21	-0.27	0.001	0.00041
1	-0.18	-0.39	0.007	0.00182
2	-0.07	-0.28	0.007	-0.00045
3	-0.17	-0.2	0.014	0.00167
4	-0.12	-0.16	0.003	0.00502
5	-0.22	-0.34	0.004	0.00152
6	-0.16	-0.04	0.005	0.00274
Mean	-0.16142	-0.24	0.005857	0.001818
Std Dev (n-1)	0.052098	0.117615	0.004180	0.001748
IDL=3*(Std Dev)	0.156296	0.352846	0.012541	0.005245

IDL = Instrument Detection Limit

APPENDIX D

Manchester Environmental Laboratory Standard Operation Procedure for the Laboratory Clean Room

MANCHESTER

ENVIRONMENTAL

LABORATORY

Standard Operating Procedure for the Laboratory Clean Room

Version 1.0

Author - William R. Kammin, Environmental Lab Director

Date - 10/27/93

QA Approval - Stuart Magoon, Quality Assurance Officer

Date

Operation of Laboratory Clean Room

1. Scope and Application

- 1.1 This SOP describes the details of the operation of room 14A, the metals "clean room", at Manchester Environmental Laboratory (MEL).

2. Historical Perspective -- Organizational Details

- 2.1 Narrative. The clean room at Manchester Environmental Laboratory is the culmination of over three years of planning by the United States Environmental Protection Agency (USEPA), and Washington State Department of Ecology (Ecology). The clean room has been designed to support sample preparation, low level standard preparation, preparation of bottles, teflon ware, filters, etc. for very low-level metals determinations. Traditionally, metals sample preparation has been plagued with contamination of the analytical blank and prepared samples, due to air particulates, metal hoods, and poorly designed sample preparation areas. Clean room technology offers solutions for many of these problems.

The heart of the lab clean room is a Clean Air Systems Corporation Class 100 clean hood. The hood is constructed from sheet polypropylene, using polypropylene welds to join surfaces. The work surface in the clean hood is a sheet of 1/8" perforated polypropylene stock. The interior of the hood is completely metal-free. Doors to the storage areas in the front of the hood have metal hinges which have been coated with white marine grade epoxy paint. The class 100 designation relates to the hood certification. The hood is certified to produce an internal environment of less than 100 particles per cubic foot. The hood is also equipped with house deionized water (DI) and vacuum services.

Air flow in the clean hood is different than most fume hoods and bears some discussion. Room air is forced through two High Efficiency Particulate (HEPA) filters mounted in the upper portion of the hood. As the air exits the HEPA filters at the top of the hood, the air flow is non turbulent (laminar), and the air is essentially particle-free. This clean air is then drawn down by the hood exhaust system over the "work" in the hood. The "work" may be a set of metals digestions on a hot plate, a drying operation, or any of a number of other sample, standard or bottle related activities. Input air through the HEPA filters is maintained at ~ 1400 cubic feet/minute (CFM), while the hood exhaust operates at ~ 1600 CFM. The slight exhaust over-velocity assures that the clean hood will maintain a slight inflow through the front few inches of the hood, thus maintaining the fume protection characteristics of the hood. So, the air flow in the hood is essentially top to bottom clean air, instead of through the front and over the work particulate laden air, as is the case in the traditional fume hood.

A discussion of other aspects of room design is in order. The walls of the room were repainted with a marine grade epoxy based "plastic" paint, to help minimize the natural shedding of paint particles from painted walls. The paint pigment is TiO_2 , and titanium is not an element of interest for most room activities. Metal floor drain covers and metal table supports were also painted with this epoxy paint. Ceiling tiles and supports are plastic, as well as door handles. Table tops and sinks in the room were fabricated from sheet

polypropylene. Metal sprinkler heads were coated with a paraffin based wax, and metal sprinkler head surrounds were coated with epoxy paint. The lighting fixtures and conduit connecting the fixtures also was fabricated from plastic materials. Wall electrical outlets were changed out to plastic materials. Hood DI and vacuum service fixtures are made of polyvinyl chloride (PVC).

When support instrumentation, the clean room remodel effort, and direct investment in the hood and teflon items are considered, the total cost of the room is over \$500,000.

There are currently three organizations at Manchester Environmental Laboratory; USEPA, Washington State Department of Ecology, and ICF Kaiser Engineers. With many potential users of the clean room, it is critical that all users follow these operational procedures.

3. Clean Room Policies

3.1 Pre-approval Policy. Before new operations are performed in the clean room, approval must be obtained from the Ecology lab director. Potential clean room operations will be evaluated for the possibility of room/hood/air contamination. Unacceptable operations are those which may significantly impact the clean room environment. Generally speaking, only samples of ambient surface, ground water, drinking water and certain effluent and mixing zone studies will be appropriate for digestion in this room. Samples containing high levels of target analytes are not appropriate for clean room preparation.

3.2 Labware. Each lab group (EPA, ESAT, Ecology) at MEL must maintain its own set of appropriate teflon labware for sample digestions. Wash bottles, forceps, and other small teflon items will be general use items, unless these items start disappearing or are contaminated by other room users.

3.3 Scheduling. Operations in the clean room will be scheduled after the review process is complete. Clean room users need to take into account the time for the approval process to occur, and be ready with alternative plans if the activity proposed for the clean room is not approved.

3.4 SOP Requirement. All activities/operations for the clean room will be supported by Standard Operating Procedures to be developed immediately after activity is approved. SOP's will conform to the user group SOP standard. SOP's will be required 30 days after activity approval. If a draft SOP for a clean room activity is not ready in 30 days, the activity will be shut down until the SOP becomes available. No exceptions.

4. Recommended Cleaning Protocols for Teflon Labware and Disposable Filters

4.1 Cleaning Protocols for Teflon Labware. The following protocol has been developed for the cleaning of the various teflon beakers, wash bottles, vials, forceps, volumetric flasks, and sample tubes which may be used in the clean room environment. The protocol should be

applicable in general to the cleaning of any plastic container (polypropylene, polyethylene, polystyrene) which may be used in the clean room environment. However, it is recommended that either FEP or PFA teflon be used for all clean room material handling operations. Currently Ecology uses 500 mL FEP teflon bottles for field sampling.

- 4.1.1 Bottle Procedure (for new Bottles). This procedure is primarily for teflon bottles, but it is applicable to any closable teflon containers, i.e., volumetric flasks, closable test tubes, etc.
- 4.1.2 Prepare 1:1 trace metals grade nitric acid by slowly adding a volume of concentrated JT Baker trace metals grade nitric acid to an equivalent volume of 18 Megohm deionized water (DI). Maintain a stock of 30 L minimum of this 1:1 acid, so that it can be used in large scale teflon bottle cleaning operations. This acid can be reused several times before it is recycled by sub-boiling distillation. Store the acid in the original concentrated acid containers, with the original contents and safety labeling still visible.
- 4.1.3 Bottle should be cleaned in batches of 25 minimum. In the clean hood, completely fill the 500 mL FEP teflon bottle with 1:1 nitric acid/DI. Allow this to leach for 72 hours minimum. Longer leaching times are acceptable.
- 4.1.4 In the clean hood and after leaching, pour the leaching acid out of the cleaned bottle back into the glass acid bottle. Rinse the bottle copiously with hood DI. After rinsing, completely fill the cleaned bottle with 18 Megohm DI. Place the cleaned and filled bottle into a zip-lock plastic bag until use.
- 4.1.5 The bottles must undergo a Quality Control check which involves testing for the analytes of interest by appropriate metals techniques. These might include Graphite Furnace Atomic Absorption (GFAA) and Inductively Coupled Plasma Mass Spectrometry (ICP/MS).
- 4.2 Disposable Filter Cleaning Procedure.
- 4.2.1 The disposable polystyrene filters are leached by adding 500 mL of the 1:1 nitric acid/DI water mixture to the filter apparatus, and allowing it to gravity filter. Preclean a minimum of 24 filters at a time.
- 4.2.2 After the gravity filtration is complete, 500 mL of 18 megohm DI water is added to the filter, and this DI is vacuum filtered through the apparatus.
- 4.2.3 After this DI is completely filtered, the filter unit is disassembled, and allowed to air dry in the Class 100 laminar flow clean hood environment.
- 4.2.4 After drying, the filters are reassembled, and the filter lids are taped securely using lab tape. Finally, the filters are placed into Zip-Lock bags to minimize possible contamination.
- 4.2.5 QA the filters by filtering 500 mL of 18 Megohm DI through a filter, and analyzing for analytes of interest by appropriate techniques.

4.3 Teflon Vial Cleaning Procedure.

- 4.3.1 Preclean a 2 or 4 L erlenmeyer flask by soaking in 1:1 trace metals grade nitric acid for 72 hours.
- 4.3.2 PFA teflon vials and screw caps are cleaned using 1:1 trace metals grade nitric acid (JT Baker) and 18 megohm DI. The vials and caps are placed in the selected flask, covered completely with the acid:water mixture, and allowed to leach for a minimum of 72 hours.
- 4.3.3 After leaching, the PFA teflon vials and caps were air-dried in the class 100 clean hood environment. The vials were then capped, batched into groups of 25, and stored in Zip-Lock plastic bags.
- 4.3.4 For field use, the vials are filled with 5 mL of 1:1 lab redistilled concentrated nitric acid/18 megohm deionized water (DI) for proper preservation of field samples.
- 4.3.5 Assess the quality of the vial cleaning process by pipetting 5 mL of concentrated nitric acid (of known "clean" quality) into a vial. Then, add the 5 mL of acid to 500 mL 18 Megohm water in a clean teflon bottle. Use appropriate analytical techniques to assess the efficacy of the vial cleaning procedure.
- 4.4 When vials, bottles and filters are cleaned for a single project, use the following protocol to evaluate the entire process of cleaning.
- 4.4.1 Four precleaned teflon (FEP) bottles are selected randomly. These bottles are already filled with 18 Megohm water from the bottle cleaning protocol.
- 4.4.2 Preservation acid from a randomly selected precleaned PFA teflon vial is added to the teflon bottle.
- 4.4.3 The acid/water mixture was then vacuum-filtered through a randomly selected Nalgene filter apparatus. The filtrate is at this point defined as a process blank.
- 4.4.4 Use appropriate analytical techniques to determine suitability of the cleaning process.

5. Special Clean Room Apparatus and Materials

- 5.1 General Considerations. Only teflon apparatus should be considered for use in the clean room. The use of teflon helps to minimize errors due to absorption losses from active sites on vessel surfaces, as well as presenting surfaces that can be reliably cleaned to minimize low-level contamination. This is true even with regard to items usually considered disposable, such as ICP or ICP/MS autosampler tubes. The initial investment in teflon will be paid back many times over by the predictable and reliable cleaning and stability properties of teflon.

5.2 Cleaning of Polyethylene Bottles for Low-level Studies. Currently Ecology uses translucent High density polyethylene (HDPE) bottles for storage of sample digestions. When using these bottles for low-level studies these polyethylene bottles need to be cleaned according to the cleaning protocol for teflon bottles (Section 4.1)

6. Reagents for Clean Room Use

6.1 Water Systems. Manchester Environmental Laboratory maintains a lab-wide DI water system. It consists of a softener/reverse osmosis unit with subsequent UV sterilization. This is the DI available in the clean hood. Following the general lab system is a dual column strong acid/strong base ion exchange system. This is used for polishing of the house DI prior to production of 18 megohm water.

The 18 megohm DI system (Millipore, Marlborough, MA) is a Milli-Q 50 system, with 2 strong acid/strong base, ion exchange columns, and activated carbon for organics removal. Use only 18 Megohm water for preparation of samples and standards in the clean room.

6.2 Acids. All acids used in the clean room for sample preparation or preservation are either JT Baker "Ultrex II" grade or redistilled in the lab sub-boiling still unit. Trace metals grade acid is appropriate for cleaning operations. See the MEL sub-boiling still SOP for details regarding operation and maintenance.

6.3 Hydrogen peroxide. Use analytical reagent grade hydrogen peroxide when digesting samples in the clean room.

7. Clean Room Operational Procedures

7.1 Operation of Clean Hood. The factory recommends that the unit be run continuously. The normal HEPA filter life is a number of years when the hood runs continuously. Continuous operation will assure a clean work area. **Lab policy is to operate the clean hood continuously.**

7.1.1 When the cabinet runs continuously, it is ready to use at all times. The work surface will, from time to time, require cleaning. Cleaning frequency will depend on hood usage. Cleaning will usually consist of rinsing the perforated polypropylene work surface with the deionized water (DI) available in the hood. If a spill of acid or sample occurs, rinse the work surface copiously with DI, and allow the surface to air dry.

7.1.2 When the cabinet is shut off for a short period of time and is turned on, the hood interior is to be wiped clean. The hood should run for 5 to 10 minutes before use when off for intervals of 1 or 2 days.

7.1.3 When the cabinet is to be off for 3 or 4 days or more, a plastic drape should be attached to the front of the hood as tightly as possible to prevent dust from entering the hood and getting into the HEPA filter. When the cabinet has been used for 2 weeks or more, the filter should be purged 1 to 2 hours.

- 7.1.4 A short interval should be allowed each time an object is set into the hood to allow loose material to be washed off the object.
- 7.1.5 Avoid fanning papers, books, arms, coats, and fast walking in front of the hood. Air currents will enter the hood and contaminate the interior. All work is performed at a minimum of six inches into the hood in order to minimize contamination due to drafts.
- 7.1.6 Spills should be cleaned up immediately. Sponge the liquid near the HEPA filter first to keep the liquid away from the filter. Should liquid splash onto the HEPA filter **DO NOT** attempt to wipe the filter. Wiping the filter will cause filter leaks. The liquid will dry, discolor and plug a small area of the filter in front. The filter is nearly 6 inches deep and a small plugged area will have little or no effect on the air flow.
- 7.1.7 Do not use the hood for storage of large objects. Large objects can disrupt the smooth laminar air flow, cause turbulent air flow behind them, and contaminated room air may be drawn into the hood. Objects should not be placed between the HEPA filter and any point where the clean environment must be maintained. A good practice is to place materials on platforms to allow air movement under, as well as around the object. All work should be performed with the operator's hands downstream of the critical process points.
- 7.1.8 After using a hotplate in the clean hood, do not store the hotplate in the hood. After a set of digestions is complete, allow the hotplate to cool to room temperature, and then remove the hot plate from the hood. The hotplate is heavy, and two or more people must be found to assist in the move.
- 7.1.9 Keep the hood sash closed when drying operations are on-going, when the hood is not in active use, or when sample digestions are occurring.
- 7.2 Before using the clean room, perform the following tasks.
- 7.2.1 Mop the floor. Wash down all table tops with DI. Rinse the perforated work bench in the clean hood with DI. Verify that your teflon sample containers have been appropriately cleaned.
- 7.2.2 Digestion pre-blank (non-digested blank to check acid water and sample container). If analyzing for zinc by ICP, prepare an acid check blank prior to sample preparation. This blank will be 20% nitric acid in 18 Megohm water. If the blank value for zinc is lower than 4 ug/L, proceed with the sample preparation. If the value of the blank is greater than 4 ug/L, determine the cause of contamination, remedy, and continue.
- 7.2.3 After using the clean room, perform the first four steps in 7.1.1.
8. Calibration and Standardization
- 8.1 Section is not applicable.

9. Calculations

9.1 Section is not applicable.

10. Quality Control

10.1 Conductivity monitoring. Conductivity of the 18 Megohm DI is monitored weekly. When using this DI, observe that the light emitting diode (LED) on the conductivity meter on the water unit itself moves to the vicinity of 18 Megohms when the unit is put into operation. If the LED does not move to a reading of 18 Megohm, the unit needs maintenance, and cannot be used for clean room purposes.

10.2 HEPA filter. The HEPA filter is expected to have a lifetime of several years, but it will eventually need replacement. No replacement schedule or criteria for replacement has been as yet developed.

11. Precision and Accuracy

11.1 Sample digestions occurring in the clean hood will be subject to same batch QC samples as a normal run. This will include spike and spike duplicate samples for the evaluation of precision and accuracy, a laboratory control sample for the evaluation of accuracy, and at least one preparation blank for the evaluation of low-level contamination.

12. Safety

12.1 General Considerations. Gloves and safety glasses must be worn at all times when working with sample digestions and cleaning operations. In the lower cabinets of the clean hood are a supply of powder free clean room gloves. Regular powdered gloves are known to contain zinc. Use only the clean room style gloves in the clean room.

12.2 All chemists must be familiar with MEL's official safety documents, including the MEL Chemical Hygiene Plan and The MEL Lab Safety and Health Manual. Copies of these documents are available for review in the Lab library.

12.3 Please note that material safety data sheets (MSDS) are available on-line from the network menu.

13. Hazardous Waste Disposal

13.1 Dispose of any hazardous waste generated in room activities in accordance with the MEL Lab Waste Disposal Manual. A copy of this document is available for review in the Lab library.

14. Bibliography/References

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