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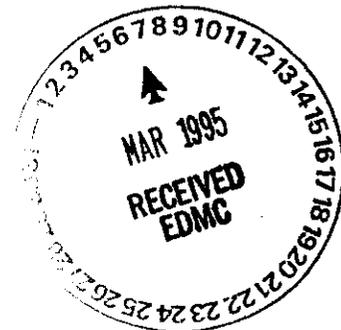
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Rev. 00

**Preliminary Determination of
Chromium Concentration Within
Pore Water and Embryonic
Chinook Salmon at Hanford
Reach Spawning Area in
Proximity to 100-HR-3 Operable
Unit**



Prepared for the U.S. Department of Energy
Office of Environmental Restoration and
Waste Management

Bechtel Hanford, Inc.
Richland, Washington



Approved for Public Release

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CONCENTRATION WITHIN PORE WATER AND
EMBRYONIC CHINOOK SALMON AT HANFORD REACH
SPAWNING AREA IN PROXIMITY TO 100-HR-3 OPERABLE
UNIT

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S. J. Hope

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CONTENTS

1.0 STATEMENT OF WORK	1
1.1 INTRODUCTION	1
1.2 OBJECTIVE	2
1.3 TECHNICAL REPORT	2
2.0 SAMPLING AND ANALYSIS PLAN	2
2.1 INTRODUCTION	2
2.2 SAMPLING LOCATIONS	3
2.3 SAMPLING METHODOLOGY/EQUIPMENT	3
2.4 SAMPLE ANALYSIS	5
2.5 FIELD DOCUMENTATION	6
2.6 QUALITY ASSURANCE/QUALITY CONTROL	6
2.7 SCHEDULE	8
2.8 SAFETY AND HEALTH	9
3.0 REFERENCES	10

FIGURES

1. 100-HR-3 Operable Unit.	11
2. Vernita Bar.	12

TABLE

1. Specific Methods, Detection Limits, Minimum Volume Requirements, Sample Preservation, and Analytical Holding Times	8
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LIST OF TERMS

AA	atomic absorption
AWQC	ambient water quality criteria
BCD	buoyancy compensator device
BHI	Bechtel Hanford, Inc.
COC	contaminant of concern
COPC	contaminants of potential concern
DOE	U.S. Department of Energy
Ecology	Washington State Department of Ecology
EPA	U.S. Environmental Protection Agency
FFS	Focused Feasibility Study
ICP	inductively coupled plasma
LOEL	Lowest Observed Effect Levels
MDL	method detection limit
OSHA	Occupational Safety and Health Administration
OU	Operable Unit
PRG	preliminary remediation goal
QMP	Quality Management Plan
QRA	qualitative risk assessment
redds	chinook salmon egg nests
SAP	sampling and analysis plan
SCUBA	self contained underwater breathing apparatus
TSS	total suspended solid

1.0 STATEMENT OF WORK

1.1 INTRODUCTION

To date, no Hanford Reach pore water/in-gravel biota data exist to support assumptions that groundwater flow path/river dilution reduces chromium concentrations below the Environmental Protection Agency's ambient water quality criteria (AWQC) for the protection of aquatic organisms, or other dose response (toxicity) criteria such as Lowest Observed Effect Levels (LOELs). This Statement of Work presents a plan to acquire river substrate water quality/contaminant data for determining the exposure and risk to ecological receptors from groundwater discharge into the river. This effort will provide groundwater/river interface information to assist 100 Area Unit Managers and Operable Unit (OU) Coordinators in their determination of groundwater cleanup levels that will be protective of Columbia River beneficial uses.

According to the 100-HR-3 OU Focused Feasibility Study (FFS) Report (DOE/RL-94-67, Draft A), the ecological receptors in the Hanford Reach of the Columbia River are potentially exposed to chromium VI (hexavalent), an ecological contaminant of concern (COC) detected in contaminated groundwater seeps at the groundwater/river interface. Chromium concentration below the AWQC of 11 $\mu\text{g/L}$, as measured in the river substrate, is considered the preliminary remediation goal (PRG) of the FFS. Iron and sulfides, which were also listed as contaminants of potential concern (COPCs), were not included as COCs. Iron concentrations detected above the chronic AWQC of 1,000 $\mu\text{g/L}$ were all taken from wells with carbon steel casings, resulting in questionable data; likewise, sulfide concentrations have only shown random detects at the detection limit (1 mg/L).

The qualitative risk assessment (QRA) for the 100-HR-3 groundwater OU (WHC-SD-EN-RA-007, Rev. 0) states that ecological receptors selected for analysis in the QRA were some of the aquatic and riparian organisms expected to be in or associated with the Columbia River. A plant, fish, crustacean, duck, and heron were used to characterize risk in the QRA. However, the ecological receptor of concern in the river, with respect to contaminant exposure for this limited investigation, is the embryonic life stage of the chinook salmon (*Onchorynchus tshawytscha*). These receptors are selected for analysis because they are non-motile and could be chronically exposed to chromium from riverbank seeps and/or subsurface groundwater discharge. The early life stages of the chinook salmon (i.e., egg, alevin, and fry) could be particularly susceptible to toxic effects from contaminant exposure because they spend a significant portion of their life cycle within or near the substrate of the Columbia River as it flows past the 100-HR-3 OU where elevated concentrations of chromium VI are in the groundwater.

The 100-HR-3 FFS report recommends that the "point of compliance" for contaminants should be the groundwater/river interface but indicates that monitoring this zone is difficult. Currently, "near-river" well data are used to assess water quality compliance. However, this results in an overly conservative indication of river water quality because it assumes no dilution in the groundwater pathway or in the river, and does not give an accurate assessment of receptor exposure in the river. This investigation will provide important data previously unobtained.

If salmon spawning areas next to the 100-HR-3 OU are susceptible to groundwater discharge exposure, it is most likely to occur during the minimal flow regime of the late autumn/early winter (time of greatest groundwater flow gradient to the river). Additionally, since fall chinook salmon

begin spawning in late October, and if chronic exposure and contaminant uptake by the embryonic salmon from groundwater discharge is occurring, then late January to early March is the appropriate time of year to sample for chromium uptake.

1.2 OBJECTIVE

The primary objective of this study is to collect pore water samples and embryonic chinook salmon from spawning sites (redds) located in the Hanford Reach of the Columbia River. Sampling for this limited investigation will focus on the river reach adjacent to the H Reactor area (100-HR-3 OU), to assess the presence and concentration of chromium within the redds. Following are the overall objectives:

- Evaluate the chromium VI concentrations in groundwater (near-river wells) and in salmon redd pore water (potential receptor contact)
- Determine if pore water chromium VI concentrations are potentially toxic to aquatic organisms
- If exposure to chromium VI is occurring, determine the results of chromium VI accumulation in embryonic chinook salmon tissue, if feasible. If chromium VI cannot be detected during tissue analysis, total chromium analysis in tissue may be substituted to determine if contaminant uptake is markedly different between samples taken from the background sample site at Vernita Bar and samples collected adjacent to the 100-HR-3 OU.

A major goal of this proposal is to determine if the second criteria of Milestone M-15-06E is achieved, whereby the chromium VI concentration in the river bottom substrates is demonstrated to be below 11 $\mu\text{g/L}$.

1.3 TECHNICAL REPORT

A technical report will be developed to present sampling procedures, findings of the laboratory analysis results, and a comparative analysis of observed pore water quality to AWQC. Data analysis of this preliminary investigation will be used to direct future studies, if needed.

Appropriate figures and tables will be included to indicate areas sampled and the results of laboratory analyses. A draft report is expected to be developed and submitted by May 15, 1995 to DOE, EPA, and Ecology for concurrent review. Following review (and comment resolution), a final report will be prepared and published by July 15, 1995.

2.0 SAMPLING AND ANALYSIS PLAN

2.1 INTRODUCTION

The principle objective of this sampling and analysis plan (SAP) is to evaluate the chromium VI

concentrations in Columbia River substrate pore water. Chromium VI levels above 11 $\mu\text{g/L}$ are known to adversely impact sensitive ecological receptors. The overall goal of the SAP is to provide sufficient contaminant data from the sampling and analysis of various media to assist project personnel in developing a profile of Hanford Reach water quality at the groundwater/river interface adjacent to the 100-HR-3 groundwater OU.

The data collected is expected to provide an approximate worst-case snapshot of the groundwater and river interactions apparent during the winter low river stage flow regime when the more sensitive embryogenesis life stage of the chinook salmon is developing.

2.2 SAMPLING LOCATIONS

Sampling locations were identified during November 13, 1994 aerial surveys to locate the fall chinook salmon redds. The salmon redds were observed to be densely clustered along the entire Hanford-side reach of river adjacent to the 100-HR-3 OU (Figure 1). Approximately 200 to 300 redds were identified along this reach as the area targeted for sampling. The Vernita Bar (Figure 2) background sampling stations were also observed to be densely clustered with redds.

Riverbank markers, surveyor stakes at the base of the bluff, and a rangefinder will be used to identify station locations (i.e., stakes and riverbank markers lined up with transect, and rangefinder distance from riverbank reference point to dive float/flag over dive sled). These measurement indicators will enable the project team to plot transects and sample points to ± 1 to 3 ft on a map.

Based on the relatively high density of redds within the Hanford Reach, pore water will be collected from up to 50 redds along the reach of the river adjacent to the 100-HR-3 OU and from 6 redds at Vernita Bar. Embryonic salmon will be collected from a subset of up to 15 of the redds sampled adjacent to the 100-HR-3 OU and from 2 of the redds sampled at Vernita Bar.

2.3 SAMPLING METHODOLOGY/EQUIPMENT

SCUBA divers will collect 400 mL pore water samples using three 140 mL hypodermic syringes per sample (420 mL total volume). To facilitate the collection of a pore water sample, a 1/2-in. x 24-in. CPVC sampling port (pipe with end-cap and orifices to capture pore water) will be inserted vertically about 18 in. deep into a redd, or the surrounding spawning gravels if the definition of a redd boundary cannot be visibly identified due to algal overgrowth or lighting conditions. The sampling port will not be installed in or behind a ridge that could potentially be capturing upstream water that is just entering the substrate. The sampling port will be installed in front of a ridge, if apparent, or in slight depressions and flat areas of the spawning gravels. The sampling port will have a cover cap to prevent any surface water (i.e., river flow) from entering it that could potentially cause a flushing action into the hyporheic zone, which could cause uncertainty about sample integrity during any followup sampling effort. The cover cap will be removed during purging/bailing of the sampling port and sample collection, and then be replaced.

The syringe sample device will be composed of two to four syringes, depending on sample volume/laboratory requirements, interconnected to nylon "T" fittings (hose barbs), Tygon tubing, and polyethylene tubing (with "O" ring seals and tubing clamps). The tubing will be inserted into the

sampling port, and the "O" ring seals will ensure that the syringe only extracts pore water and excludes water from the water column above the substrate (i.e., water that could potentially be drawn down space between the 3/8-in. outside diameter of tubing and 1/2-in. inside diameter of sampling port). The first syringe will be actuated to draw 5 to 6 volumes of pore water through the tubing to bail/evacuate the sampling tube and bottom of sampling port. A tubing clamp will be closed and the bailing syringe will be disconnected from the syringe sample device and purged into the river. The syringe will then be reconnected, the clamp will be opened, and another 5 to 6 volumes of pore water will be bailed and purged. This bailing/purging will be conducted three times to ensure that no surface water will cross-contaminate the pore water sample. Next, the other sample syringes will be actuated, one at a time, to draw out samples of pore water (through the filter) slowly until each syringe is filled. After the syringes are filled, the tubing clamp will be closed to prevent the transfer of water into or out of the sample syringe device. The syringe sample device will then be pulled out of the sample port and placed in a mesh diver's bag, and a diver will transfer it to the sample technician on the riverbank. The samples will be stored in a cooler at 4 °C until delivery to the laboratory for analysis. If water clarity conditions allow, underwater photos and video will record the sampling procedures. The sampling port will be labelled with an identifier number (e.g., Redd 01, 02, etc., that can be cross-referenced to a sample tracking number) and left in place should subsequent sampling be required to verify detection of chromium.

The polypropylene syringes are Monoject non-sterile (clean/single use) 140 mL units typically used for veterinary medicine. The clear vinyl tubing (ID 1/4 in. x OD 3/8 in., with 1/16 in. wall thickness) is non-toxic Food and Drug Administration-approved material. The Tygon tubing, with the same dimensions as the clear vinyl tubing, meets the necessary QA/QC standards. The Quanterra and PNL laboratories have tested blanks and known chromium standard solutions from the syringe sample devices, and indicated acceptable results for the proposed analysis of chromium.

Embryonic chinook salmon will be collected by a certified fisheries scientist experienced in working with Pacific Northwest salmon species. Embryonic salmon will be collected by hand excavating a redd until the embryonic salmon are exposed. The minimal volume of embryonic salmon required for laboratory analysis (about 100 g) will be removed from the nest. The sample will then be transferred to the sample technician who will label the sample container and store the sample in a cooler at 4 °C until it is transferred to the lab for analysis. The redd gravel will be replaced as close as feasible to its original configuration.

Pore water sampling will be conducted during the first round of sampling followed by the sampling of embryonic salmon. During pore water sampling, separate syringe samples will be collected for field instrument measurement of conductivity.

Sampling and monitoring of the near-river wells and seeps will be coordinated with the in-river pore water sampling to provide additional comparative data points for chromium contaminant concentrations. The planning for this sampling effort recognized the dynamic nature of the interaction between contaminated groundwater underlying the Hanford Site and Columbia River water. Consequently, interpreting the analytical results from interstitial water samples will consider the variability likely to be introduced by daily river stage fluctuations and seasonal water table conditions. This sampling effort represents an important contribution to the objectives of TPA Milestone M-30-05 ("to perform long-term evaluation of Columbia River and unconfined aquifer interaction").

Groundwater samples were collected in early December 1994 from the 183-H Solar Basins well

network. Samples from other 100-H Area wells were obtained in late December as part of the 100-HR-3 operable unit semiannual sampling program. The chromium VI travel time between the wells nearest the river and the nearshore river channel is probably on the order of months. Consequently, analytical results from well samples collected in December should suffice for comparisons with riverbed sediment interstitial water sample results collected in January and February. However, travel time estimates through the zone of interaction between the aquifer and the river are uncertain, as a result of the fluctuating river stage.

Groundwater seepage observed along the riverbank might be more closely related to interstitial water in nearshore riverbed sediments. Riverbank seepage samples will be collected along the Hanford Site shoreline adjacent to the interstitial water sampling locations. Seepage samples will be collected during low river stage and when the electrical conductivity of the seepage is significantly different from nearshore river water. Samples will be collected using a peristaltic pump, following procedures established earlier for riverbank seepage sampling (DOE/RL-92-12).

Groundwater seepage is also monitored hourly at two locations along the 100-H Area shoreline. Temperature/conductivity probes are buried in shoreline gravels and connected to data loggers. These stations have operated under the TPA Milestone M-30-05 program for approximately the past year and provide an excellent record of the water quality changes that occur in the riverbank as a result of the fluctuating river stage. They will continue to operate during this sampling effort.

2.4 SAMPLE ANALYSIS

Pore Water

Pore water analysis will be conducted by Battelle PNL using Adsorptive Stripping methodology using Voltammetry (AdSV) and will serve as the primary analytical method for measuring the levels of chromium VI in the pore water. The minimum detection level for chromium VI in the pore water using the AdSV method is estimated at $0.50 \mu\text{g/L}$ ($\pm 0.10 \mu\text{g/L}$).

Additionally, approximately 20% of the samples collected will be analyzed using EPA Standard Methods. The Quanterra Environmental Services Laboratory will work to optimize the analysis system to attain the lowest detection limit below the MDL of $6 \mu\text{g/L}$. Presently, laboratory calculations indicate that a detection level of $1.20 \mu\text{g/L}$ is achievable.

Approximately 60 samples of pore water will be forwarded to the laboratories for analysis of chromium VI. Approximately three samples of pore water will be collected and forwarded to the laboratories for analysis of total chromium (a frequency of one sample for every twenty sample locations). Field duplicates of pore water will be collected at a frequency of one duplicate for every ten locations sampled. Field blanks of deionized water collected in the type of syringe used to collect pore water and taken underwater will be submitted to the laboratories to provide an indication of potential field and laboratory contamination. A minimum of one duplicate for each sample type will be collected and submitted for analysis to provide an indication of field and laboratory precision. Split samples of pore water will be provided to Ecology for independent analysis.

Pore water will be collected and submitted to the laboratory and analyzed for total and chromium VI using EPA Test Methods for Evaluating Solid Waste (SW-846), 3rd Edition, Final Update I

procedures. Information on specific methods, detection limits, minimum volume requirements, sample preservation, and analytical holding times are provided in Table 1. The laboratory will prepare and analyze internal QC samples including method blanks, matrix spikes, and duplicates as indicators of contamination, accuracy and precision. Internal laboratory QC samples will be prepared and analyzed at a frequency consistent with the requirements of the applicable referenced method.

Embryonic Salmon

Embryonic salmon will be submitted to a laboratory (TBD) for analysis of total chromium. Field duplicates of embryonic salmon will be at a frequency of one duplicate for every ten locations sampled.

2.5 FIELD DOCUMENTATION

Standard Hanford Site procedures will be followed for labeling samples, documenting samples collected, and documenting sample transfer to and from the laboratory. A scientific collection permit has been approved by the Washington Department of Fish and Wildlife to collect embryonic chinook salmon from the Hanford Reach of the Columbia River. The permit will be in the possession of the boat/dive team at the sampling sites.

A field logbook will be used to log samples collected and transferred to the laboratory for analyses. Chain-of-Custody forms will be used for sample transfers. Since sample transfer from the divers to the workboat will probably be accomplished by lowering and raising sample containers in a basket/mesh bag, syringe sampling devices and embryonic salmon sample containers will be labelled prior to sampling to prevent errors in sample handling and storage.

If water clarity conditions allow, underwater photos and video will be taken to document pore water and embryonic salmon sampling procedures.

2.6 QUALITY ASSURANCE/QUALITY CONTROL

Pursuant to the requirements of DOE/RL-90-28, Rev. 2, the following criteria have been selectively invoked for this activity using a graded approach. The criteria are controls described in the BHI Quality Management Plan (QMP).

The QMP has been prepared and is implemented in compliance with the DOE/BHI Contract DE-AC06-93RL12367 AND DOE document DOE/RL-90-28, Rev. 2, *Environmental Restoration Quality System Program Requirements For The Hanford Site*. Commensurate with the Program/Policies promulgated by the QMP, BHI will manage its work to ensure TPA requirements and other commitment documents and laws are satisfied in a timely manner.

The controls are implemented by qualified personnel as described in this Statement of Work and implemented by EPA-reviewed environmental investigation procedures (EIPs) contained in BHI-EE-01, *Environmental Investigations Procedures*. Examples are listed below with each specified QMP criterion.

BHI QMP (Part 2, Section C) criteria:

Criterion 11 - Process Control- Work process with respect to sample collection shall be controlled to ensure that they are accomplished by qualified personnel (e.g., EIP 1.3, "Indoctrination, Training and Qualification").

Criterion 12 - Sample Control- Procedures that control the documenting and tracking of sample possession from collection through handling, preservation, shipment, transfer, storage analysis and disposition shall be implemented (e.g., EIP 3.0, "Chain of Custody").

Criterion 13 - Control of Measuring and Test Equipment- Tools, gauges, instruments, laboratory equipment, measuring and test equipment, and standards used in the collection/analysis of samples described in this statement of work shall be properly identified, controlled, and maintained (e.g., BHI-SH-05, *Industrial Hygiene Desk Instructions*).

Criterion 14 - Handling, Storage, Shipping and Disposal- Packaging, handling, storing, shipping, and preserving of samples shall be accomplished in a manner that prevents damage and/or loss, minimizes deterioration, and provides for final disposal (e.g., EIP 3.1, " Sample Packaging and Shipping").

Criterion 15 - Field and Laboratory Inspection and Test Control- BHI procedures shall be used for the following:

1. Inspecting or otherwise verifying operations for collecting/analyzing data (e.g., EIP 2.5, "Data Package Validation Process").
2. Controlling tests performed in the field/laboratory (e.g., BHI-EE-01, all Section 5.0 Field Sampling EIPs).
3. Indication of inspection, test, or operating status of items/samples (e.g., EIP 1.5, "Field Logbooks").

Table 1. Specific Methods, Detection Limits, Minimum Volume Requirements, Sample Preservation, and Analytical Holding Times.

Water Matrix						
Analyte	Method	Methodology	Preservative	Holding Time	Volume	MDL
Chrome (Total)	6010	ICP	HNO ₃ to pH <2 Cool 4 °C	6 months	G 400 mL	20 ^a µg/L
Chrome (Hex)	7196	AA	Cool 4 °C	24 hours	G 400 mL	1.2 ^b µg/L
Chrome (Hex)	AdSV	Stripping Voltammetry	Cool 4 °C	24 hours	G 10 mL	0.5 ^c µg/L
Embryonic Salmon Matrix						
Chrome (Total)	6010	ICP	Cool 4 °C	6 months	G 1 g ^d	1.2 ^b µg/L

AA - atomic absorption.

ICP - inductively coupled plasma.

MDL - method detection limit.

^aInformation provided is the SW-846 Estimated Quantitation Limit. Instrument Detection Limits for the current quarter are < 10 µg/L.

^bThe Quanterra, Inc. laboratory will work to optimize the analysis system to attain the lowest detection limit below the MDL of 6µg/L. Presently, laboratory calculations indicate that a detection level of 1.2 µg/L is achievable.

^cPNL detection limit using AdSV analytical method.

^dDry weight.

2.7 SCHEDULE

Sampling will occur during the winter (preliminary target dates: January 30 to February 28, 1995). If weather or other conditions preclude sampling during the aforementioned target dates, sampling will be extended into March 1995. The schedule is driven by the following factors:

- River flow regime and water levels controlled by power generating demands from upstream (Priest Rapids Dam) hydroelectric generating stations.

- Fall chinook salmon of the Hanford Reach begin spawning in late October, and if there is an exposure and uptake of chromium VI by the embryonic salmon, then late January to early March would be the appropriate time of year to sample.
- The turbidity/total suspended solid (TSS) load of the river is probably approaching its lowest level during the winter, providing relatively good underwater visibility.
- The pace of the sampling activity will be somewhat governed by the effects of cold water and flow/turbulence on the divers. The variability in water temperature and flow velocity (river level) is not expected to adversely affect the objective of this investigation. However, the project team has contacted the operators of the Priest Rapids Dam to request their assistance in controlling river flows during diving operations.

2.8 SAFETY AND HEALTH

Diving work will be performed in accordance with Occupational Safety and Health Administration (OSHA) Standards for Commercial Diving, 29 CFR 1910, Subpart T. A copy will be maintained at the dive location.

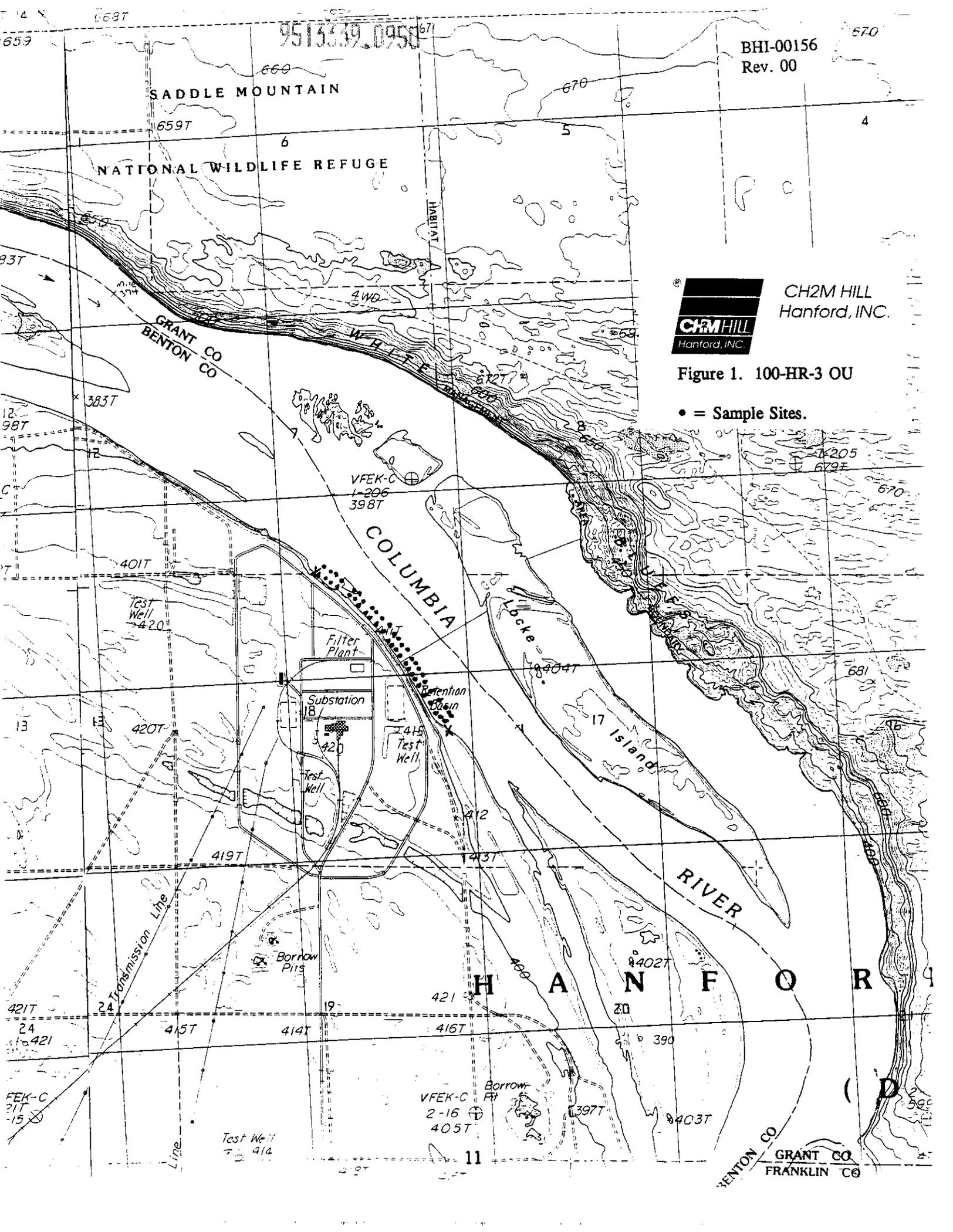
The divers (Steve Hope, CH2M HILL, a certified fisheries scientist; and Frank Cobb, consultant) are certified in the use of SCUBA by nationally recognized organizations and have past experience with river dives in turbulent flow regimes. Both divers will be in the water for the sampling event. Each diver will wear appropriate dive gear (drysuits with thermal liners) for cold-water diving. Each diver will have at least two regulators to provide primary and backup on-demand air supply. Each diver will wear a buoyancy compensator device (BCD) that can be automatically (and manually) inflated to assist the diver in adjusting buoyancy and keep the diver afloat in any emergency situation. Both divers will ascend to the workboat or riverbank when the air tank pressure of either diver reaches 300 psi. Safety and health personnel will stand by with life jackets, life-rings, and first-aid equipment to assist the divers as needed.

Dives are not expected to exceed 35 ft in depth; therefore, diver decompression should not be a concern during ascents to change air tanks or pass samples to the workboat personnel.

The workboat will be anchored under power in the river or beached as appropriate for the area being sampled. In accordance with Washington Department of Fish and Wildlife requirements, the vessel will display a sign that reads "RESEARCH", readable at 100 yd to unaided vision. The boat will have an anchor of sufficient design and weight to keep it secured at a sample station. The boat will display a large diver's flag at all times to indicate to other boat traffic that divers are in the water. The boat operator will also keep a watch for boat traffic encroaching on the area where divers are working, and warn off boats approaching too closely to the work area.

3.0 REFERENCES

- BHI-SH-05, *Industrial Hygiene Desk Instructions*, Bechtel Hanford, Inc., Richland, Washington, February 1995.
- BHI-EE-01, *Environmental Investigations Procedures*, Bechtel Hanford, Inc., Richland, Washington, February 1995.
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- DOE/RL-94-67, Draft A, *100-HR-3 Operable Unit Focused Feasibility Study*, U.S. Department of Energy Richland Operations Office, Richland, Washington.
- WHC-SD-EN-RA-007, Rev. 0, *Qualitative Risk Assessment for the 100-HR-3 Groundwater Operable Unit*, Westinghouse Hanford Company, Richland, Washington.



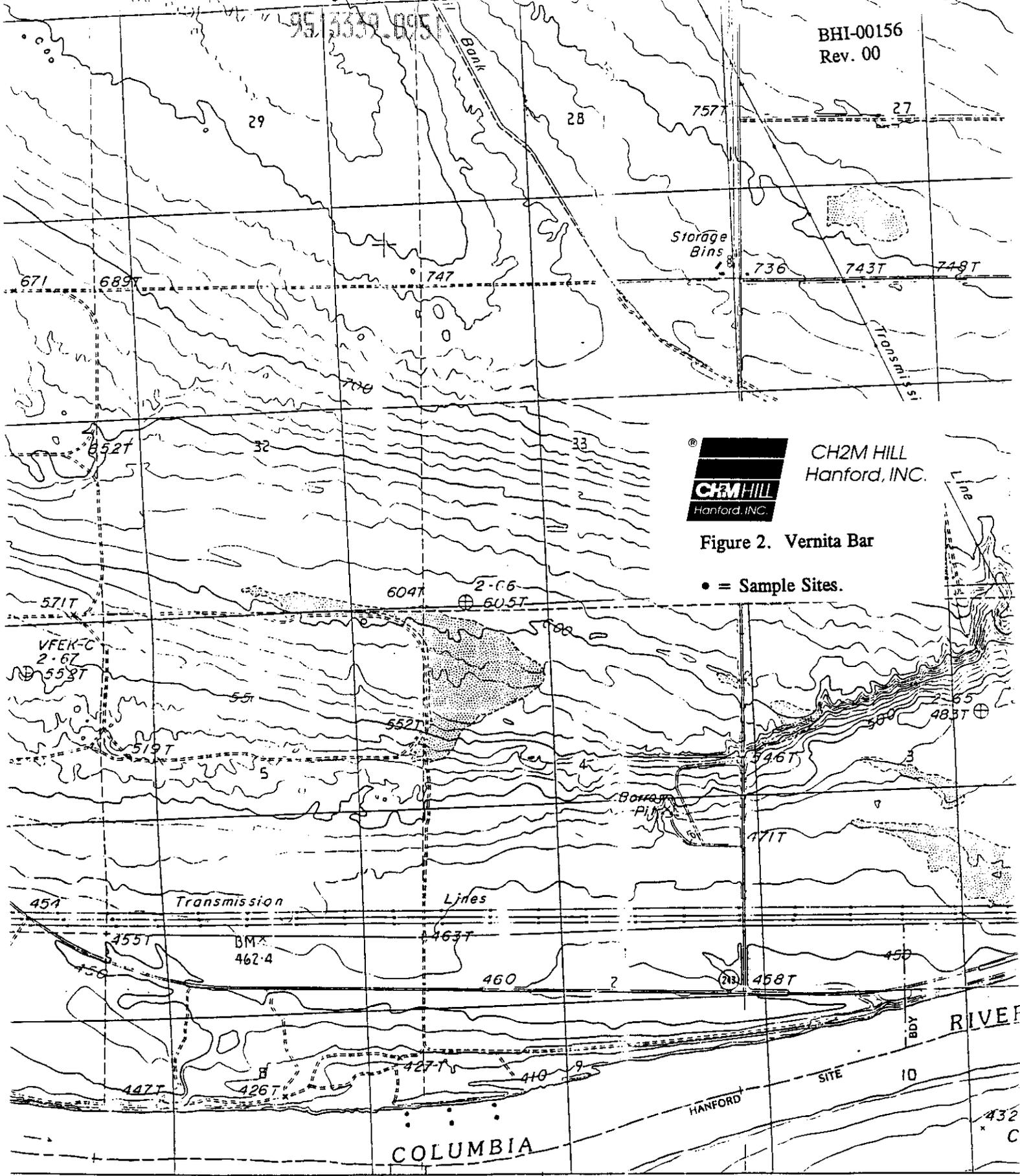
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Figure 1. 100-HR-3 OU

• = Sample Sites.

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FRANKLIN CO

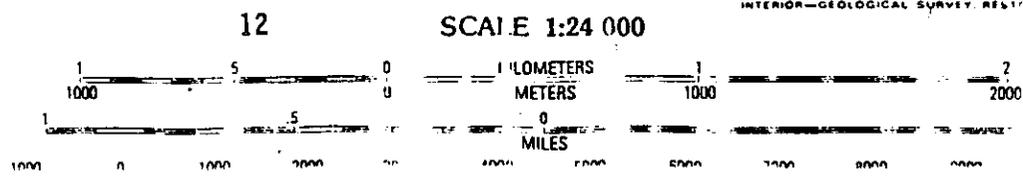


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Hanford, INC.

Figure 2. Vernita Bar

• = Sample Sites.

TOPOGRAPHICAL SURVEY
USGS, NOS/NOAA
1982
1986
CONFORMAL CONIC
PROJECTION, ZONE 11
NORTH, SOUTH ZONE



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