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Department of Energy
Richland Operations Office
P.O. Box 550
Richland, Washington 99352

JAN 24 1995

Mr. Douglas R. Sherwood
Hanford Project Manager
U.S. Environmental Protection Agency
712 Swift Boulevard, Suite 5
Richland, Washington 99352-0539

Dear Mr. Sherwood:

U.S. ENVIRONMENTAL PROTECTION AGENCY (EPA) EXPEDITED REVIEW COMMENTS ON "PRELIMINARY DETERMINATION OF CHROMIUM CONCENTRATION WITHIN PORE WATER, PERIPHYTON, AND CHINOOK SALMON EGGS AT HANFORD REACH SPAWNING AREA IN PROXIMITY TO 100-HR-3 OPERABLE UNIT," BHI-00156, REV. 0A, NOVEMBER 1994

Thank you for expeditiously reviewing the subject document and providing comments contained in the EPA letter dated December 12, 1994. EPA's involvement during the preliminary design phase of this effort was helpful in developing a representative sampling technique as well as a concrete detection level for Cr^{+6}. Finally, it is the U.S. Department of Energy, Richland Operations Office's (RL), understanding that the data obtained by this effort must satisfy the Hanford Federal Facility Agreement and Consent Order requirements for data collection. RL's detailed responses to EPA's comments are attached.

If you desire to discuss this matter further or require additional information, please contact Mr. Randy Brich at 376-9031.

Sincerely,

Julie K. Erickson, Director
River Sites Restoration Division

RSD:RFB

Attachment

cc w/attach:
S. M. Alexander, Ecology
L. E. Gadbois, EPA

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RESPONSE TO EPA EXPEDITED REVIEW COMMENTS ON PRELIMINARY DETERMINATION OF CHROMIUM CONCENTRATION WITHIN PORE WATER, PERIPHYTON, AND CHINOOK SALMON EGGS AT HANFORD REACH SPAWNING AREA IN PROXIMITY TO 100-HR-3 OPERABLE UNIT

General Comments

1. Water Sampling:

A method to accurately sample the water in the hyporheic zone has been of longstanding concern. This has led to each of the Tri-Parties concluding that near-river wells will be used to evaluate exposure risk (100-BC-5, 100-KR-4, and 100-HR-3 qualitative risk assessments) and for points of compliance for remedial actions (100-BC-5, 100-KR-4 and 100-HR-3 proposed plans). The document under review (BHI-00156) identifies a plan to attempt sampling of the hyporheic zone. This deviates from the "near-river-well" approach that has been in place for several years. This is the most high interest aspect of this proposed investigation. For water data from this sampling to be useful, there are several key aspects to its credibility that must be defendable:

(A) That the water samples represent the water environment in which both salmon eggs develop, and the young salmon are exposed to during their first few months of life within the cobble on the river bottom.

(B) If salmon are able to sense the localized contaminated groundwater upwelling areas, and avoid use of those areas for their redds, then contaminated groundwater could be reducing their spawning habitat but not appear to show any impacts in the results of this study.

In response to item (A), the document appears to represent a valid attempt to collect water from the hyporheic zone in the near proximity of salmon eggs. The salmon alevin are considerably more sensitive than the eggs to hexavalent chromium, and the assessment will not provide specific information as to whether or not the alevin have a selectivity regarding groundwater upwelling areas. Selectivity by adult salmon (item "B" above) may be different than selectivity by the alevin.

<u>Response</u>:

A field pore water sampling method has been developed to ensure that the water sampled represents the water environment in which the salmon eggs develop and young salmon are exposed to during the first few months of life within the cobble on the river bottom. The response to Specific Comment No. 8 discusses the sampling methodology that will be implemented to ensure that the appropriate water sample is collected.

All efforts will be made to establish sample sites within salmon redds and within gravel/cobble substrates that appear to be suitable spawning habitat that would be selected by adult salmon. The ability to distinguish the boundary definition of a redd will depend on factors

such as; (1) ambient light conditions at depth, (2) river turbidity at the time of the sampling event, and (3) the amount of algae growth that possibly recovered the substrate that was cleaned/turned over during nest excavation by the salmon.

2. River Stage:

Related to item A in comment 1, river stage, both on a seasonal and daily pattern, affects the rate of groundwater discharge into the Columbia River. Salmon eggs and larva may be exposed to months of groundwater discharge, yet this sampling is a single "snap-shot" in time of this dynamic process. For groundwater sampling in the operable units (probably a much more stable regime relative to the inter-cobble regions of the river bottom) the Tri-Parties have conducted multiple rounds of sampling spanning the annual cycle in addition to considerable historical data, to form a cleanup decision basis for the groundwater operable units. The single sampling identified in the document for review, if successful, should be viewed as a potential starting point for a monitoring program that can then start to feed into the cleanup decision process.

In earlier discussions with DOE, we have pointed out the importance of coordinating this sampling with concurrent measurements in the near-river wells for the 100-H area. In discussions since, we are told that this coordination is planned, but this is not indicated or detailed in the document. Thus, we have no opportunity to provide specific comments on this coordination.

Response:

The Environmental Restoration Contract (ERC) Project Team understands that the results of this field investigation may require followup monitoring and is planning accordingly. The ERC Project Team will coordinate with the Tri-Parties for the development of future work plans related to this task. 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 Hanford Federal Facility Agreement and Consent Order (Tri-Party Agreement) Milestone M-30-05 (i.e., "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 1994, as part of the 100-HR-3 operable unit semiannual sampling program. The hexavalent chromium 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 February 1995. 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 localities. 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 Richland Operations Office 1992).

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 Tri-Party Agreement 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.

3. Egg Age:

The female salmon that lay the eggs are new arrivals to the Hanford Reach and have not had much opportunity to accumulate any Hanford contaminants. Presumably the eggs are relatively "pristine" in regard to Hanford contaminants. As they age in the Hanford Reach gravels, they may begin to accumulate contaminants. The age of the egg (since being laid) is important in the evaluation of egg contaminant-burden information.

In a brief presentation to the Hanford Natural Resource Trustees on December 8, 1994, it was indicated that the sampling was now planned for early January 1995. This appears to represent a best attempt to allow the eggs to equilibrate with their surroundings.

Response:

The ERC Project Team is considering postponement of embryogenesis life stage (salmon egg) sampling until after the pore water sampling is completed. Preliminary laboratory results would then be available that could indicate Cr^{+6} concentrations in the hyporheic zone are potentially toxic to alevins/fry. The postponement would allow the dive team to focus their initial efforts on setting up pore water sample sites and collecting samples. A late-February/early-March 1995 sampling effort, later in the embryogenesis life stage (i.e., alevins/fry) which is more sensitive to Cr^{+6} than eggs, could be focused on a hyporheic zone that may have a Cr^{+6} concentration considered lethal/sub-lethal to this receptor.

4. Analytical Detection Limit (Water):

Chromium is the high-interest contaminant. Its most toxic form, Cr^{+6}, has a chronic water criteria value of 11 ppb. The analytical detection limit must be well below that, so that values slightly less than 11 ppb have a small uncertainty associated with them.

Response:

Both internal and external discussions indicated the need for a detection level, together with its associated uncertainty, that is far below the ambient water quality criteria value of 11 μg/L for Cr^{+6}. Since the standard method for Cr^{+6} analysis has limitations, a search for a different technique, capable of producing much lower detection limits, was initiated. This search resulted in the determination that Adsorptive Stripping methodology, using voltammetry (AdSV), will serve as the primary analytical method for measuring the levels of Cr^{+6} and total Cr in the pore water. The minimum detection level for Cr^{+6} in the pore water using the AdSV method is estimated at 0.50 μg/L ($\pm$ 0.10 μg/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 minimum detection limit (MDL) of 6 ug/L. Presently, laboratory calculations indicate that a detection level of 1.2 ug/L is achievable.

5. Analytical Detection Limit (Salmon Egg and Periphyton Tissue):

There is no indication of the tissue burdens that are toxic to either of these two organisms. There is also no indication of what contaminant levels in these tissues means to other organisms up their food chain. Both those types of information are needed to evaluate the appropriateness of the 150-200 ppb MDL.

Response:

Periphyton sampling has been eliminated from this field investigation due to the lateness in the season to sample an adequate quantity for analysis. The author of the subject statement of work acknowledges that there is no indication of the tissue burdens that are toxic to either periphyton or salmon eggs. However, bioassay data exists discussing the effects of exposure of the embryogenesis life stage of salmon to Cr^{+6}, which is of interest to the Project Team in the determination of exposure risk to this sensitive ecological receptor (Becker 1990, and Eisler, 1986). Based on this information and the uncertainties about toxicity effects, a comparison of background (Vernita Bar) Cr^{+6} tissue uptake concentrations to 100-HR-3 concentrations may yield information indicating a potential exposure risk that could be adverse to the sensitive embryogenesis life stage of the salmon (i.e., late egg stage development and/or alevin/fry stage).

NOTE: The Project Team obtained chinook salmon eggs from the Priest Rapids Hatchery for tissue analysis by the Quanterra Environmental Services Laboratory to determine the lowest MDL achievable. The MDL of 150-200 ppb reported in the subject statement of work was based on an estimate derived from the standard method used to analyze the pore water. It is anticipated that the analysis of the egg tissue will yield a lower MDL that could be more readily compared to the results of earlier toxicity studies conducted at Hanford as reported in Becker, 1990.

6. Station Location:

A method is needed to identify station locations relative to groundwater plume discharge areas. The document indicates that stations will be selected adjacent to 100-HR-3 in the general area of the groundwater plume. We support that approach. Within this stretch of river, there may be areas of greater and or lesser discharge, and these areas of discharge may or may not be correlated with the location of salmon redds. Work done according to this document will not resolve this issue.

Response:

Riverbank markers, surveyor type stakes at the base of the bluff, and a rangefinder will be used in conjunction with a Global Positioning Satellite (GPS) system on the boat to identify station locations (i.e., stakes and riverbank markers lined up with transect, rangefinder distance from riverbank reference point to dive float/flag over dive sled, and boat GPS reading a known distance [100-150 feet] upstream of dive sled). These measurement indicators will probably enable the Project Team to plot sample points to ± 1 to 3 feet on a map.

Specific Comments

7. Page 2, Section 1.3, 2nd paragraph:

The document states that: "It is anticipated that a draft report will be developed for submittal to DOE by April 1, 1995. A subsequent draft for review by the EPA and Ecology is anticipated by May 1, 1995." We would encourage DOE to do a concurrent review on this technical report.

Response:

DOE will conduct a concurrent review of the technical report.

8. Page 3, Section 2.3, 5th-6th lines:

The document states that: "polyethylene tube insert will ensure that the syringe only extracts pore water and excludes water from the water column above the substrate". This is our #1 technical concern with the field work. Specifically:

(A) Our understanding is that a stiff teflon tube is to be attached to the syringe and inserted into the gravel/cobble, but this is not stated in the document. The specifics of this are important for a number of reasons: the tube may be deflected from a cobble and thus not be sampling from the correct depth, the insertion of the tube may dilute the hyporheic zone with the intrusion of river water, if water is withdrawn rapidly it may suck down river water (especially if there is little pore volume in that area), etc.

(B) A redd is a depression in the bottom of the river bottom. The downstream edge is in a sense a ridge that projects into the flow of the river. This ridge will intercept a relatively high river energy that is apt to help drive river water into the bottom cobble. This will act to dilute upwelling groundwater. Thus the downstream edge of the redd may not represent the same groundwater/river-water mix as is present in the central portion of the redd.

Response:

The flexible tube insert, that was previously demonstrated to agency personnel, has been eliminated in favor of a more reliable design and sample collection methodology as explained in the following discussion.

The sample collection method of extracting pore water from the substrate is a method that was recently developed by the ERC Project Team. The syringe extraction method was developed and bench tested to ensure that when a pore water sample is drawn from the interstitial substrate, it does not draw in surface water. The bench test procedure included insertion of the syringe tubing with "O" rings into the sampling port (PVC pipe @ 1/2" x 24"). Water was pored into the space (void) between the ID of sampling port and OD of tubing (1/8" space). The sampling port was vertically submerged in a deep tub, and when the syringe plungers were withdrawn, the syringes filled with tub water without drawing down the water column within the void in the sampling port, indicating a tight "O" ring seal. Water pressure on the interior/exterior surfaces of the syringe, including the tightly fitting plunger seal, will be equal at all depths which will prevent intrusion of surface water into the sample volume. The syringe is transparent which will allow the diver/sampler to view the water sample entering the body of the syringe and observe any abnormalities that could occur. The sampling devices are composed of inert plastic and rubber materials, and no metal fittings that could cross-contaminate a sample are used. During revision of the Sampling and Analysis Plan, the methodology will be revised to state the following:

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 inch x 24 inch CPVC sampling port (pipe with end-cap and orifices to capture pore water) will be inserted vertically about 18 inches 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. Taking into consideration the topography of the river bottom, 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 replaced.

The syringe sample device will be composed of four syringes (two syringes for the Pacific Northwest Laboratory [PNL] lab) interconnected to nylon "T" fittings (hose barbs), polyethylene tubing (with double "O" ring seals and a tubing clamp), and an EPA approved 0.45 micron filter. The tubing will be inserted into the sampling port and the two "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" outside diameter of tubing and 1/2" 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 opened, and another 5 to 6 volumes of pore water will be bailed and purged. This bailing/purging procedure will be conducted three times (for a total of 15 to 18 volumes of purging) to ensure that no surface water will cross-contaminate the pore water sample. Next, the other three syringes (one for the PNL lab) 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, placed in a mesh divers bag, and transferred to the sample technician on the riverbank by a diver. 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 in the event that future sampling is desired to verify an earlier detection of chromium. The sampling port will also be marked externally with depth-in-inch indicators to verify its depth in the substrate.

The polypropylene syringes are Monoject non-sterile (clean/single use) 140 ml units normally used for veterinary medicine purposes. The clear vinyl tubing (ID 1/4" x OD 3/8", with 1/16" wall thickness) is non-toxic F.D.A. approved material. 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.

In response to comment (B); the depression is the upstream edge of a redd. The redd (nest) is actually below or somewhat behind the ridge described. Thus the downstream edge of the redd could represent the same groundwater/river-mix as is present in the central portion of the redd.

If you desire, please contact Randy Brich at 376-9031, at your convenience, and arrangements will be made to bring the syringe sampling device and sampling port to your office for a demonstration.

9. Page 3, Section 2.3, 2nd paragraph:

We support the attempt to do some field screening (if feasible) for conductivity in an attempt to identify groundwater upwelling areas.

Response:

The dive team (samplers) will make every effort to implement some field screening for conductivity into the field investigation, if feasible. The present plan is to collect at least one syringe sample (140 ml) per transect for conductivity measurements to be measured with field instruments by the onsite sample technician.

10. Page 6, Water Cr^{+6} MDL:

See general comment #4 for more detail. Adverse effects occur at very low concentrations, and a "solid" detection limit near the 1.2 ug/l is needed.

Response:

According to Quanterra Environmental Services Laboratory calculations, a Cr^{+6} detection level of 1.2 ug/L is achievable for the Standard Method and PNL indicates that 0.5 ppb is easily achievable via the AdSV methodology.

11. Page 7, top few paragraphs:

This document, especially this section, provides a very sketchy description of the analytical specifics that are crucial to support future use of this data. In other forums (not expedited reviews of a sampling and analysis plan such as this) we have worked extensively with DOE to develop the detail needed to defend our field work. It is incumbent on DOE to ensure that those steps for defensibility are built into this sampling and analysis plan. The plan does not provide the detail, nor is an expedited regulator review adequate to ensure the credibility of this work effort. Of particular concern is the citation of the BHI Quality Management Plan as the basis for the QA/QC. We have not seen nor reviewed this document. It is incumbent on DOE to compare this BHI Plan with the EII manuals to which we have devoted considerable effort. We do not intend to start all over again with the BHI Quality Management Plan and redo what we went through with the EII manuals.

Response:-

The laboratory procedure detailing the AdSV method used to measure the Cr^{+6} concentration in pore water is available for review. Additionally, Jerry Yokel, State of Washington Department of Ecology, observed a demonstration of the method and indicated that it would be acceptable in the determination of Cr^{+6} levels in pore water. If you would like a demonstration of the method please contact Randy Brich at 376-9031, at your convenience, and appropriate arrangements will be made.

Quality Assurance/Quality Control: Pursuant to the requirements of DOE/RL-90-28, REVISION 2, the following Criteria have been selectively invoked for this activity using a Graded Approach. The Criteria are controls described in the Bechtel Hanford, Inc. (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, Revision 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 assure Tri-Party Agreement 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 via EPA reviewed environmental investigation instructions (EIIs) contained within the BHI-EE-01 Environmental Investigations Procedures Manuals. 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 assure that they are accomplished by qualified personnel. (e.g., EII-1.7, Indoctrination, Training and Qualification)

Criterion 12 - Sample Control - Procedures which control the documenting and tracking of sample possession from collection through handling, preservation, shipment, transfer, storage analysis and disposition shall be implemented. (e.g., EII 5.1 Chain of Custody/Sample Analysis Request)

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., EII 3.2 Calibration and Control of Monitoring Instruments)

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., EII 5.11 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., EII 1.12 Performance Audit)

2) controlling tests performed in the field/laboratory (e.g., BHI-EE-01, Section 5.0 Field Sampling EIIs)

3) indication of inspection, test or operating status of items/samples (e.g., EII 1.5 Field Logbooks).