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Evaluation of Chromium Speciation and Transport Characteristics in the Hanford Site 100D and 100H Areas

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

Westinghouse
Hanford Company Richland, Washington

Management and Operations Contractor for the
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EVALUATION OF CHROMIUM SPECIATION AND TRANSPORT CHARACTERISTICS IN THE HANFORD SITE 100D AND 100H AREAS

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Field and laboratory investigations have been conducted to define the fate and transport characteristics of chromium contamination present in the 100D/H Areas of the Hanford Site. This information is relevant to assessing the impact of the release of hexavalent chromium to the Columbia River associated with the discharge of groundwater from the Hanford unconfined aquifer. Included in this study was the determination of the concentration and aqueous speciation of chromium in the unconfined aquifer, and an assessment of potential changes in speciation as groundwater passes through the river/aquifer transition zone and mixes with the Columbia River.

The fate of chromium was evaluated through the determination of chromium speciation of water samples collected from the Hanford unconfined aquifer, from seeps along the river, and from the river itself. The potential for uptake of chromium in the riverbed and riverbanks resulting from interaction with organic matter and oxide components associated with sediments was assessed by characterization of riverbank sediment samples. Mixing tests involving chromium-contaminated groundwater and river water were also conducted to determine if alteration of chromium speciation could occur subsequent to entering the Columbia River. In addition, groundwater plume maps were prepared from existing monitoring data of the 100-D and 100-H Areas to provide information regarding groundwater flow paths and potential chromium sources.

The results of this study indicate that chromium present within the Hanford unconfined aquifer of the 100-D and 100-H Areas is predominantly in the hexavalent oxidation state. Chromium is apparently relatively stable in the oxidized form owing to the lack of organic matter within the aquifer. A portion of the chromium is removed as groundwater passes through the river/aquifer transition zone due to reduction and precipitation associated with sediment/water interaction processes. Chemical data collected from seep water samples, however, suggests that most of the hexavalent chromium ultimately discharges into the Columbia River. Dilution of hexavalent chromium subsequently occurs during the mixing of groundwater and river water, with relatively little change taking place in speciation.

OVERVIEW

- Objectives of Study
  - Define chromium speciation of 100 D/H groundwater
  - Assess potential changes in chromium concentration and speciation as groundwater flows through aquifer/river interface and mixes with Columbia River
- Approach
  - Define current chromium distribution patterns
  - Determine chromium speciation of water samples
  - Characterize riverbank sediments
  - Perform groundwater/river laboratory mixing tests

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ENVIRONMENTAL CHEMISTRY OF CHROMIUM

- Chromate or Hexavalent Chromium
  - CrO_4^{2-} is predominant hexavalent chromium species
  - Toxic and mobile
  - Utilized as corrosion inhibitor and decontaminant

- Reduction from Hexavalent to Trivalent Oxidation State

$$CrO_4^{2-} + 8H^+ + 3e^- \rightarrow Cr^{3+} + 4H_2O$$

- Important Reductants in Environment
  - Organic matter
  - Ferrous iron

- Trivalent Chromium
  - Nontoxic, natural form of chromium
  - Cr^{3+} immobilized by precipitation and adsorption

$$Cr^{3+} + 3OH^- \rightarrow Cr(OH)_3$$

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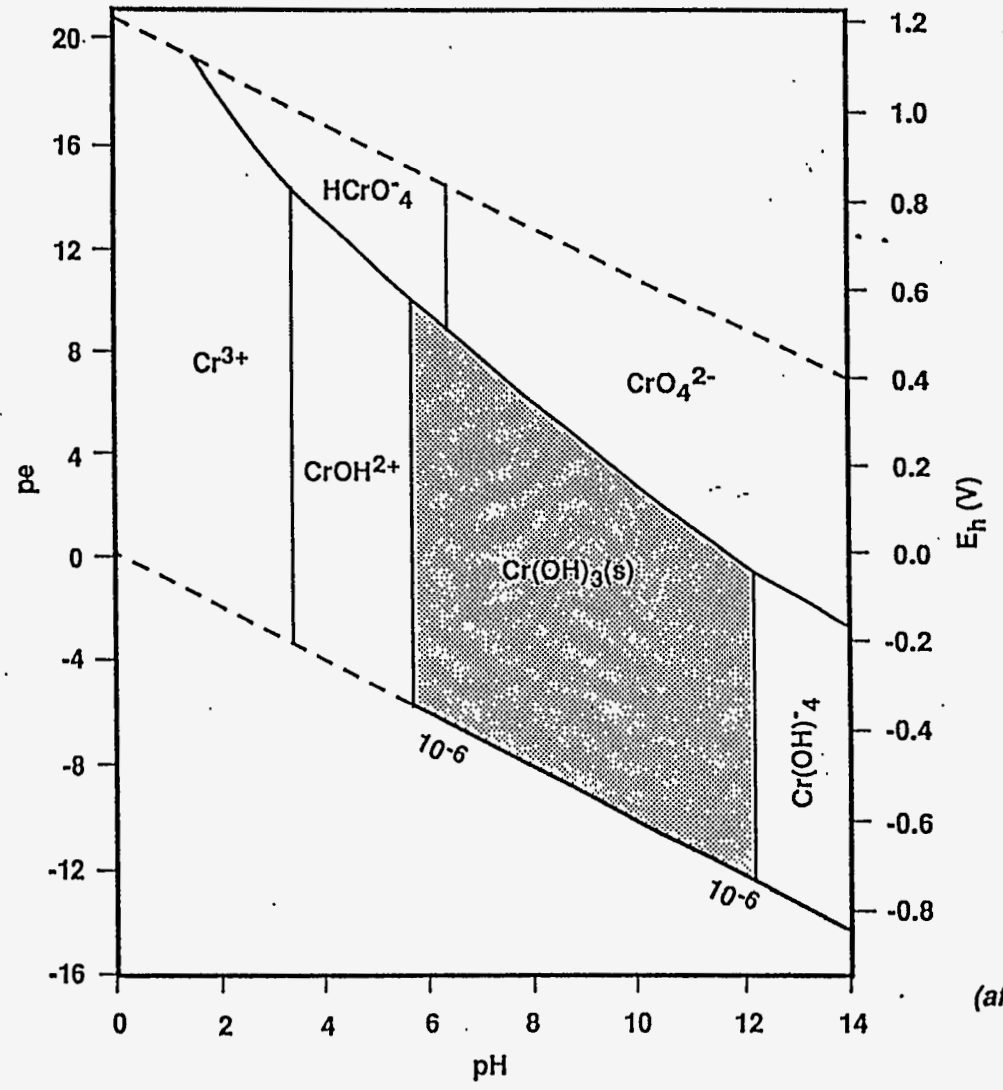
pe-pH Relationships for Chromium Species



(after Richard and Bourg 1991)

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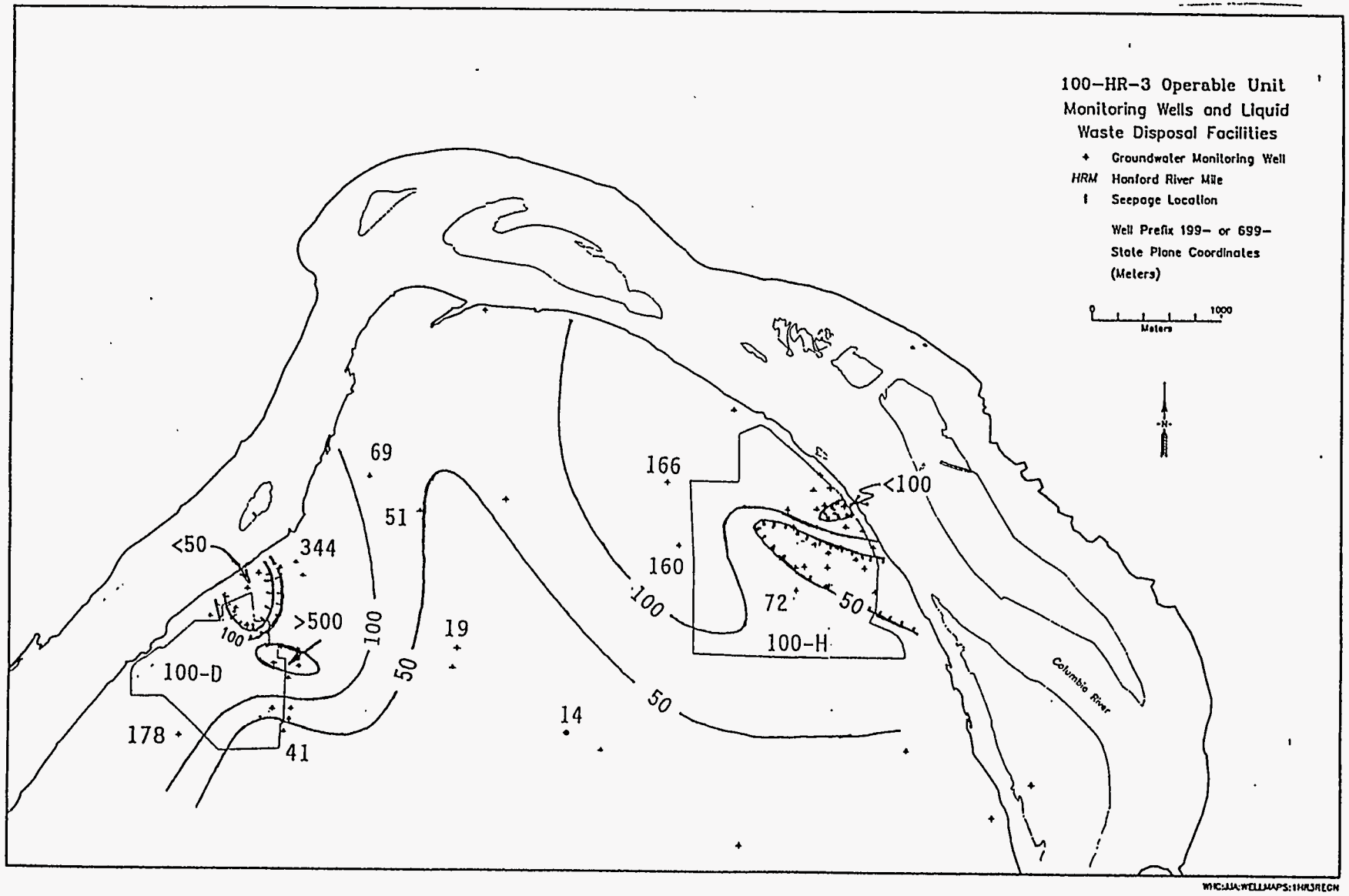
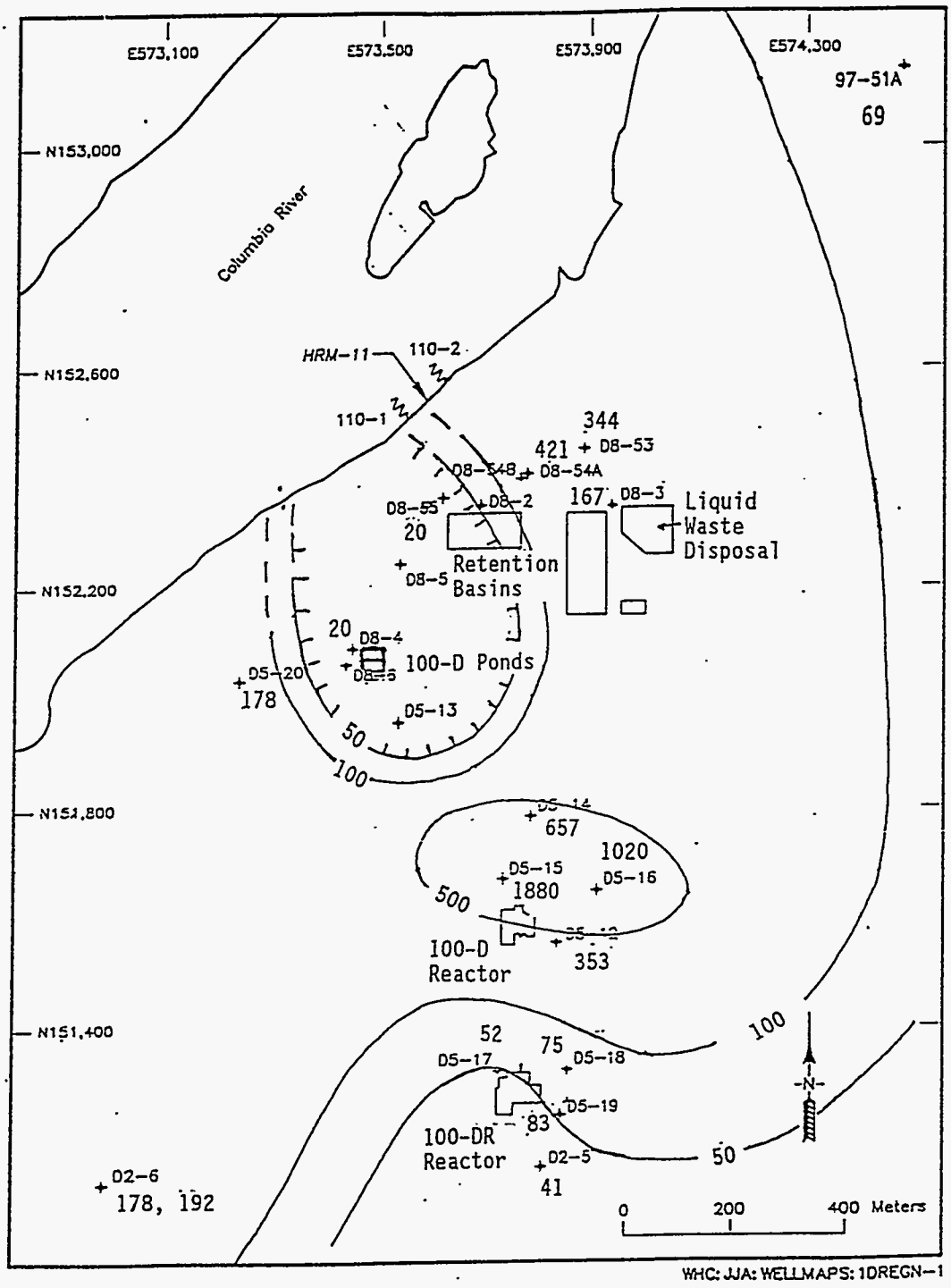
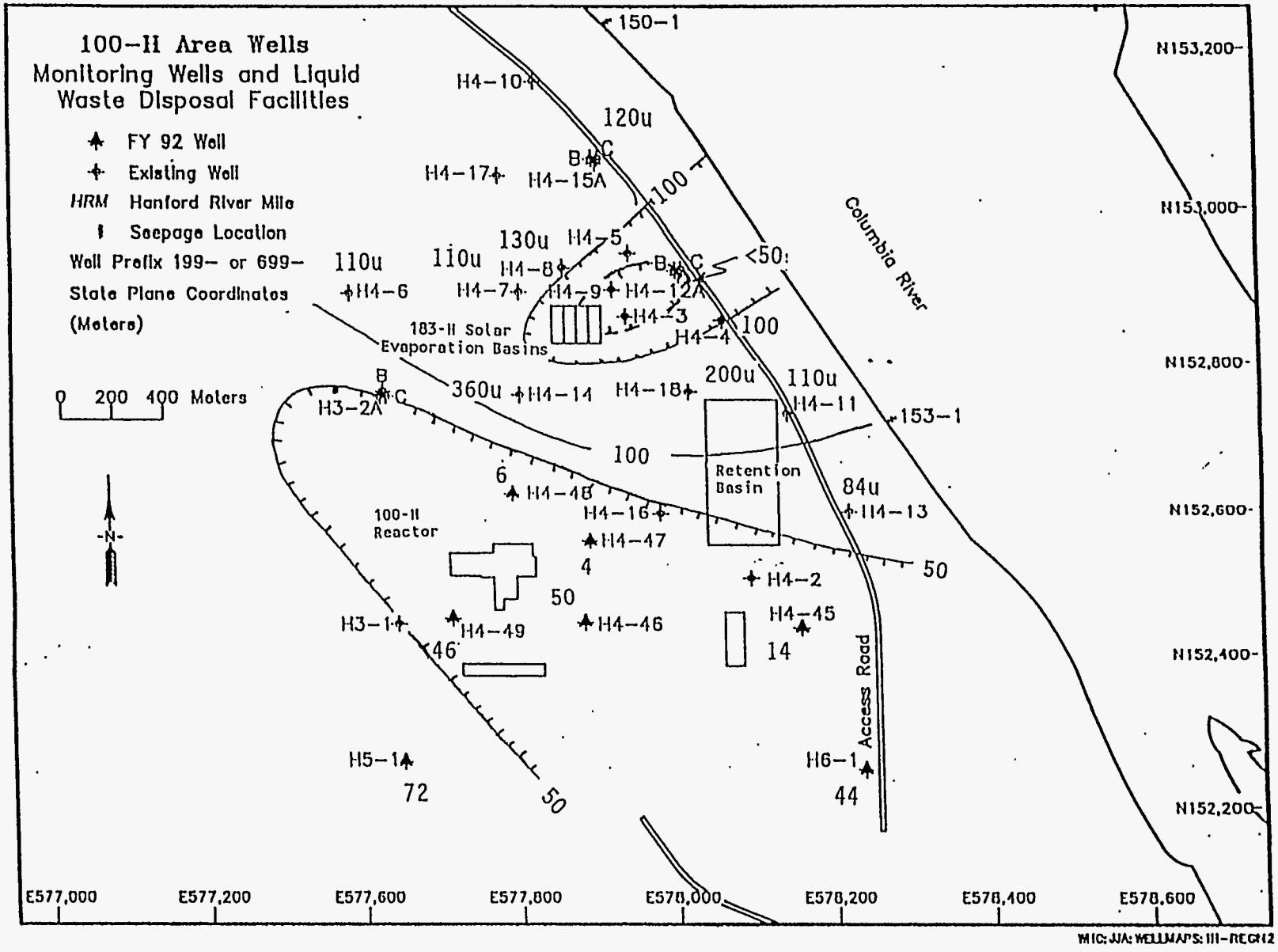


Chromium Distribution in the Hanford Site Unconfined Aquifer of the 100-D and 100-H Areas. Data shown is total chromium concentration values in ppb for filtered groundwater samples collected in October of 1992.



Chromium Distribution in the 100-D Area. Data shown is total chromium concentration values in ppb for filtered groundwater samples collected in October of 1992.



Chromium Distribution in the 100-H Area. Data shown is total chromium concentration values in ppb for filtered groundwater samples collected in September through November of 1992, and unfiltered samples (indicated by u suffix) collected in October of 1992.

CHROMIUM CONCENTRATION AND SPECIATION OF WATER SAMPLES

- Samples Collected
  - Groundwater from unconfined aquifer of 100D/H Area
  - Seeps and drive point locations along river
  - Columbia River water samples
- Analysis of Water Samples
  - Total chromium and other cations/metals by ICP (CLP)
  - Hexavalent chromium by spectrophotometer (7196)
  - Chromium speciation of river and seep samples also performed by Cranston and Murray method
  - Anions, nitrite-nitrate, pH, conductivity, TOC, and TIC analytical data also acquired using EPA methods

Hexavalent and Total Chromium Analytical Data (mg/L) for Groundwater Samples Collected in the 100-D and 100-H Areas.

Well #	Date Time	Cr(VI), 7196 unfiltered	Cr(VI), Hach	Cr_T, ICP	Cr_T, Hach
D5-15	7/13/93 08:47	--	1.26f	--	1.85uf 1.80f
H4-4	7/13/93 09:40	--	0.05f	0.075uf B08QZ0	0.05uf 0.05f
H4-3	7/13/93 10:15	--	0.13f	0.180uf B08QY9	0.18uf 0.16f
D5-15	5/13/94 09:20	1.65 B0BML3	1.1f 1.2f 1.45f	1.59uf B0BML1 1.40f B0BML2	1.45f
D5-15 (dup)	5/13/94 09:25	1.66 B0BML6	1.6f 1.3f	1.65uf B0BML4 1.50f B0BML5	1.3f
D5-16	5/13/94 11:15	--	0.78f 0.81f	--	0.80f
D8-53	5/13/94 12:00	0.41 B0BML9	0.32f 0.35f 0.34uf 0.38uf	0.329uf B0BML7 0.368f B0BML8	0.36f 0.35uf
H4-14	5/13/94 13:30	<0.05 B0BMM2	0.04f 0.04f	0.053uf B0BMM0 0.051f B0BMM1	0.03f
H4-11	5/13/94 14:22	<0.05 B0BMM5	0.06f 0.06f	0.064uf B0BMM3 0.066f B0BMM4	0.05f
H4-12C	5/13/94 15:00	--	0.26f 0.27f	--	0.24f
Equipment Blank	5/13/94 16:00	<0.05 B0BMM8	0.00f 0.00f	≤0.004uf B0BMM6 ≤0.004f B0BMM7	0.00f

WHC sample numbers are indicated by B0 prefix.
f = filtered sample
uf = unfiltered sample
-- not analyzed
All samples analyzed by EPA SW-846 Method 7196 were unfiltered.

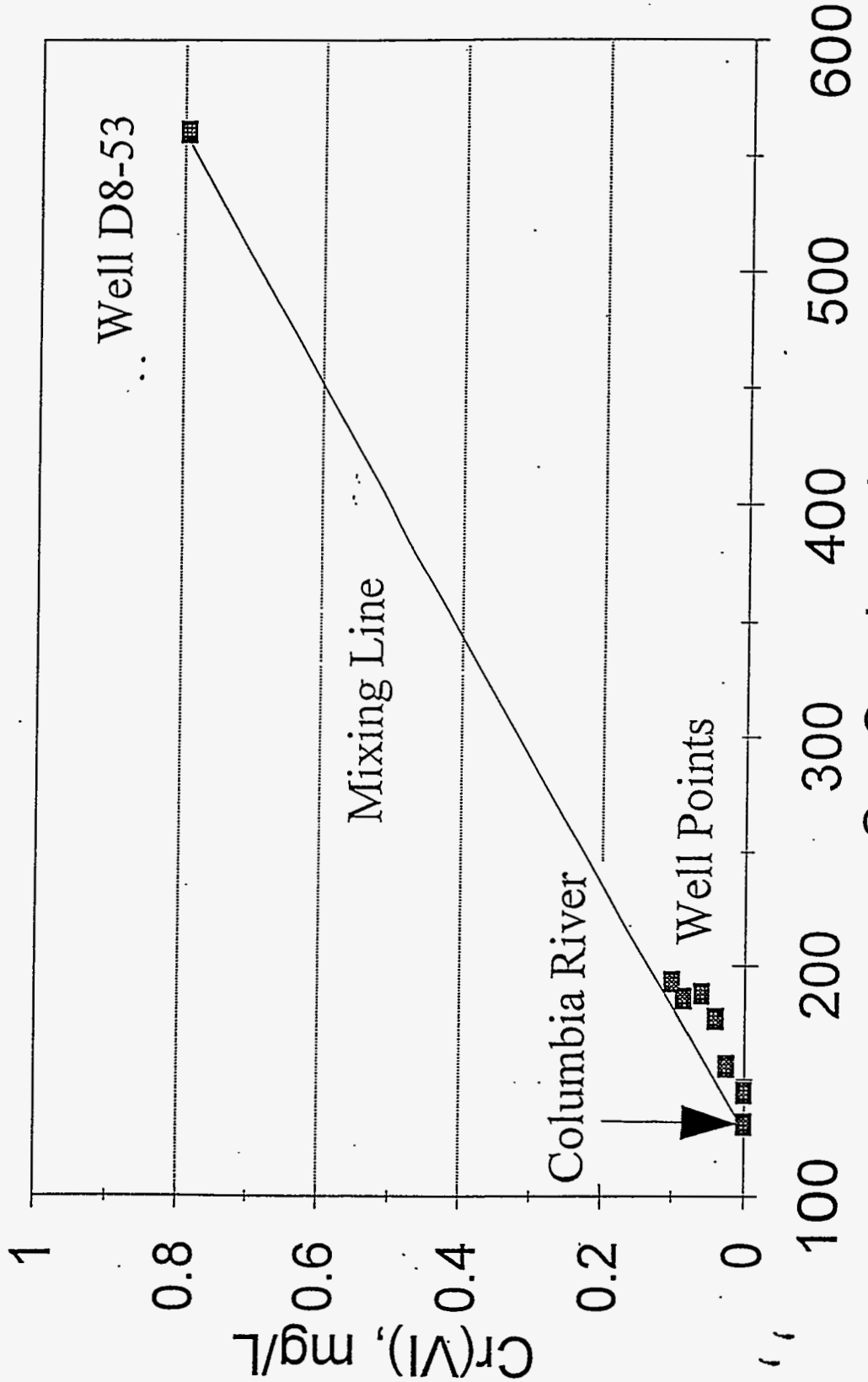
Hexavalent and Total Chromium Analytical Data (mg/L) for Seep Samples Collected in the 100-D and 100-H Areas.

Location	Date Time	Cr(VI), 7196 unfiltered	Cr(VI), Hach	Cr_T, ICP
Seep 153-1	3/17/93 08:30	--	0.03uf 0.05uf	0.045uf B08BD1 0.050f B08BD2
Seep 110-1	3/26/93 10:00	--	0.14uf	0.276uf B08BD7 0.247f B08BD8
Seep 110-1	3/31/94 09:15	<0.05 B0BMJ8	0.03uf	0.026uf B0BMJ6 0.025f B0BMJ7
Seep 110-1	4/1/94 08:00	<0.05 B0BMK1	0.01uf	0.025uf B0BMJ9 0.016f B0BMK0
Well Pt #5	4/1/94 09:00	<0.05 B0BMK4	0.01f	12.7 uf B0BMK2 0.022f B0BMK3
Seep 110-1 (dup)	4/1/94 9:45	<0.05 B0BMK7	0.02f 0.02uf	0.020uf B0BMK5 0.021f B0BMK6
Equipment Blank	4/1/94 11:30	<0.05 B0BML0	0.00f	≤0.003uf B0BMK8 ≤0.004f B0BMK9

Hexavalent and Total Chromium Analytical Data (mg/L) and Conductivity (μs/cm) of Drive Point Water Samples Collected at 100-D.

Location	Date Time	Cr(VI), WHC 7196	Cr_T, Hach	Cond, μs/cm
Well Pt #1	3/31/94 10:15	0.08uf 0.09uf	0.12uf 0.13uf	183 188
Well Pt #2	3/31/94 10:30	0.06uf 0.06uf	0.14uf 0.14uf	187 188
Well Pt #3	3/31/94 10:35	0.04uf 0.04uf	0.12uf 0.14uf	177 176
Well Pt #4	3/31/94 10:40	0.00uf 0.00uf	0.10uf 0.09uf	145 144
Well Pt #5	3/31/94 11:00	0.02uf 0.03uf	0.10uf 0.10uf	155 157
Well Pt #6	3/31/94 11:10	0.10uf 0.10uf	0.18uf 0.18uf	193 193

Cr(VI) versus Specific Conductivity for Well Point Water Samples.



RESULTS OF CHROMIUM SPECIATION STUDIES

- Chromium Speciation of Groundwater Samples
  - Elevated chromium in filtered samples represents dissolved hexavalent chromium
  - Unfiltered samples often contain reduced chromium associated with particulate matter

- Chromium Speciation of Seep and Drive Point Samples
  - Dissolved chromium is predominantly in the hexavalent oxidation state
  - Data suggests Cr(VI) is conserved during groundwater/river mixing

- Chromium Speciation of Columbia River Samples
  - Total dissolved chromium ~0.25 ppb at 100D
  - Total dissolved chromium 0.55 ppb near 100H, ~80% Cr(VI)

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CHARACTERIZATION OF RIVERBANK SEDIMENTS

- Approach and Objectives
  - Four sediment samples collected near seep 110-1 of 100D Area
  - Determine concentration and speciation of chromium in sediments
  - Assess interaction processes between riverbank sediments and groundwater
- Characterization and Testing Methods
  - Mineralogical/textural analyses by XRD
  - Semi-quantitative PIXE chemical analysis
  - Extraction and dissolution tests
  - Batch sediment/solution interaction tests

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RESULTS OF SEDIMENT STUDIES

- Sediment Characterization Results
  - Texturally sands with minor clay/silt fraction
  - Composed primarily of quartz and feldspar plus kaolin/serpentine, mica/illite, and smectite
  - Moderately enriched in chromium (85 to 145 ppm)
- Implications
  - Minor uptake of chromium by sediment occurs as groundwater passes through riverbank
  - Chromium precipitates as a result of reduction by labile iron and organic matter in sediments
  - Most chromium probably passes through riverbank mixing zone relatively unaltered, however

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GROUNDWATER/RIVER MIXING STUDY

- Objective
  - Evaluate potential changes in speciation or concentration of dissolved chromium as groundwater discharges into the Columbia River

- Approach
  - River water composite prepared from samples collected at 10 locations (~40 liters)
  - Composite mixed with chromate-contaminated groundwater from well D5-15 at various ratios
  - Controls and mixtures analyzed for Cr(VI) and other constituents at the beginning of each test and at 4 hours, 1 day, 3 days, 7 days, and 21 days

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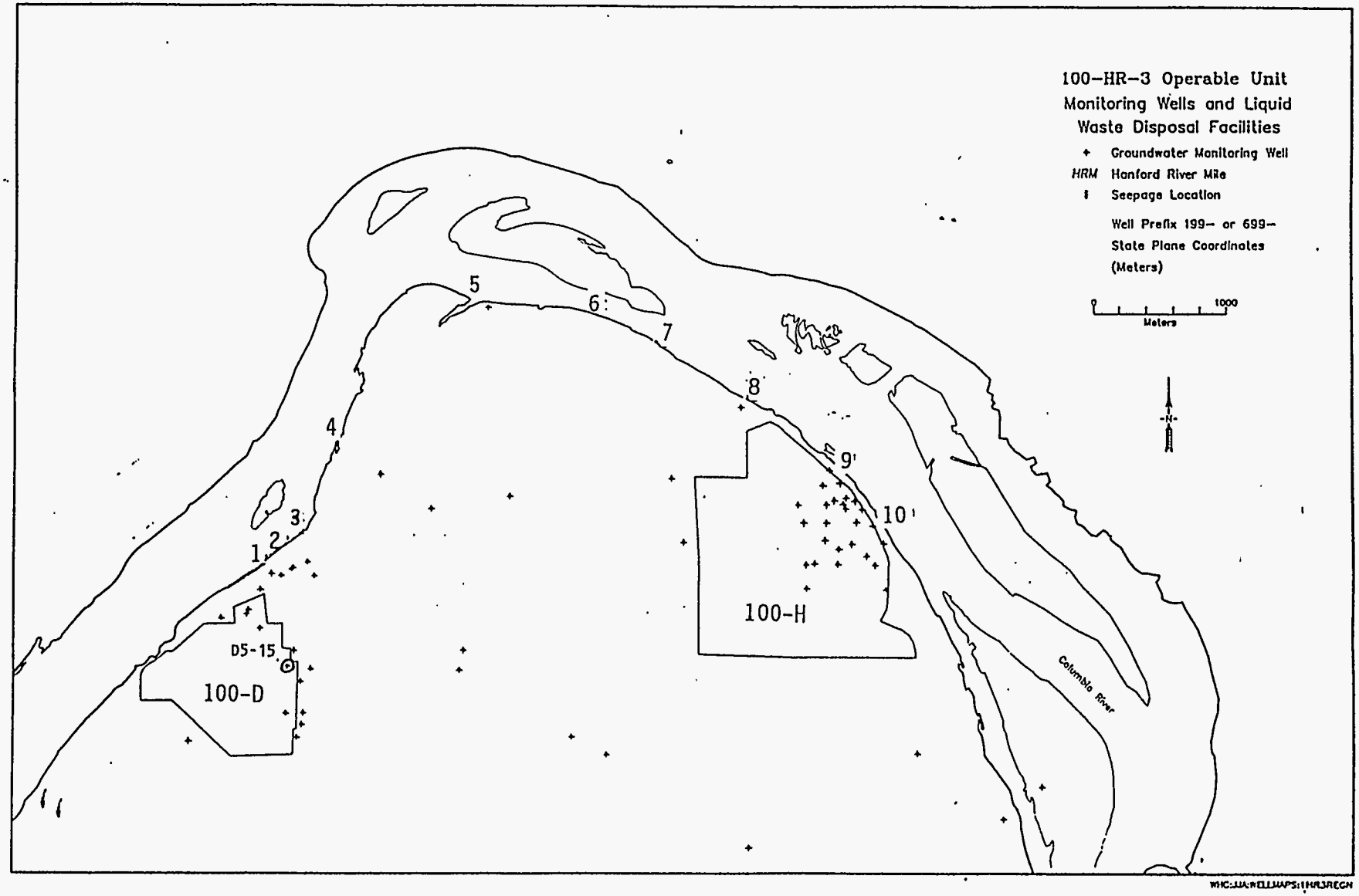
Sampling Locations for Columbia River Composite.



DESCRIPTION OF TESTS PERFORMED

Test 1 - River water control (no chromium)
Test 2 - River/groundwater ratio = 1
Test 3 - River/groundwater ratio = 10
Test 4 - River/groundwater ratio = 100
Test 5 - River/groundwater ratio = 500
Test 6 - River/groundwater ratio = 10, mixture exposed to UV light to evaluate photooxidative effects
Test 7 - 2000 ppb Cr(VI) standard solution added to river water at a river/solution ratio = 10 to evaluate groundwater matrix effects
Test 8 - D5-15 groundwater control, 1600 ppb Cr(VI)
Test 9 - Filtered groundwater and river water combined at a river/groundwater ratio = 10 to evaluate effect of suspended particulate matter on Cr(VI) concentration

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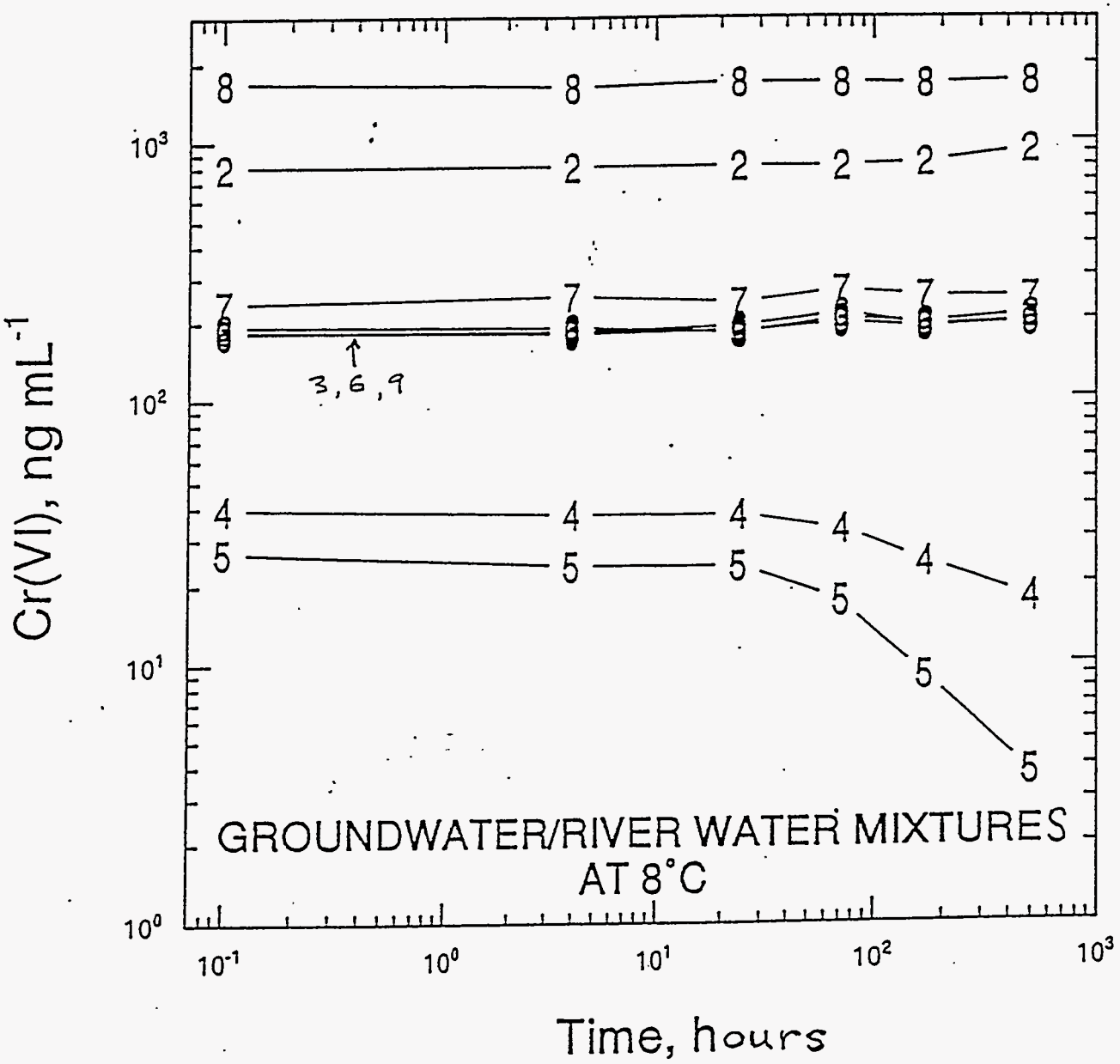
Cr(VI) Concentration versus Time for Mixing Tests.



RESULTS OF MIXING TESTS

- Principal Observations
  - Little change observed in chromium concentration or speciation during laboratory mixing tests conducted at lower river/groundwater ratios
  - Possible decrease observed in chromium concentration during tests conducted at higher ratios
- Implications
  - Chromium will remain largely in the hexavalent state after entering the Columbia River
  - Chromium concentration decreases in river primarily in proportion to dilution, although some reduction and precipitation probably occurs at high dilutions

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CONCLUSIONS

- Dissolved chromium present in groundwater and seeps is primarily in the hexavalent oxidation state.

- A minor portion of chromium is reduced and precipitated on riverbank sediments as groundwater passes through the groundwater/river interface, but this is unlikely to be an important sink for chromium.

- Chromium remains in the hexavalent oxidation state after groundwater mixes with the Columbia River and varies in concentration primarily in proportion to the degree of dilution.

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