Quality Assurance Project Plan

Effects of Small-Scale Gold Dredging on Metals Concentrations in the Similkameen River

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July 2004

303(d) listings addressed in this study:

Similkameen River (WA-49-1030) - Arsenic

Ecology EIM number: AJOH0045

Approvals

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Abstract

A plan is described for obtaining metals and ancillary water quality data on the impact of smallscale gold dredges operating on the Similkameen River, a tributary to the Okanogan River in North Central Washington State. The metals of interest are arsenic, copper, lead, and zinc. Approximately 70 samples of dredge effluents, the dredge plume, and ambient river water will be collected. Clean sampling techniques and low-level analytical methods will be used.

Background

The Similkameen River is located in North Central Washington (Figure 1). During the public comment period on the Similkameen River Arsenic TMDL (Peterschmidt and Edmond, 2004), concerns were raised by the community and the Colville Confederated Tribe regarding the potential impact of small-scale gold dredging on arsenic concentrations in the river. An earlier laboratory simulation conducted by the Washington State Department of Ecology (Ecology) had concluded that metals concentrations would be rapidly diluted downstream of a dredge (Johnson, 1999). The applicability of these data to field conditions was called into question.

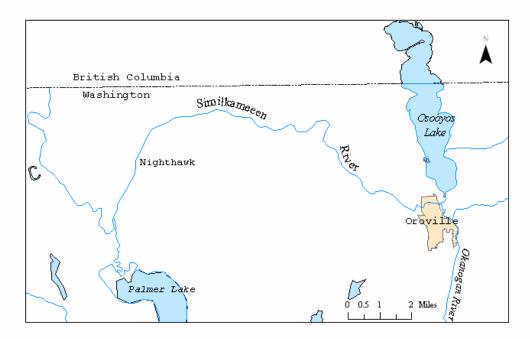


Figure 1. The Similkameen River

Dredging activities have been traditionally allowed on the Similkameen under mineral prospecting leases from the Washington State Department of Natural Resources (DNR). It is hard to quantify the amount of dredging activity that goes on. The Ecology Central Regional Office (CRO) has observed 20 or more rigs along the river at one time, although only a few of them were in operation (Mark Peterschmidt, Personal Communication). There are no restrictions on where dredging can be done.

The Department of Fish and Wildlife (WDFW) is the lead agency regulating small-scale mining and prospecting. Their *Gold and Fish* pamphlet constitutes the Hydraulic Project Approval permit that small-scale prospectors and miners must comply with when conducting activities covered in the pamphlet. Exceptions to the pamphlet, authorization for other mining and prospecting activities, or use of other equipment types than authorized by the Gold and Fish pamphlet can be granted through issuance of a written Hydraulic Project Approval. Among other regulations in the *Gold and Fish* pamphlet, WDFW requires a minimum 200-foot separation between dredges. The role of Ecology in this activity is to administer water quality standards to prevent interferences with, or harm to, beneficial uses of the river.

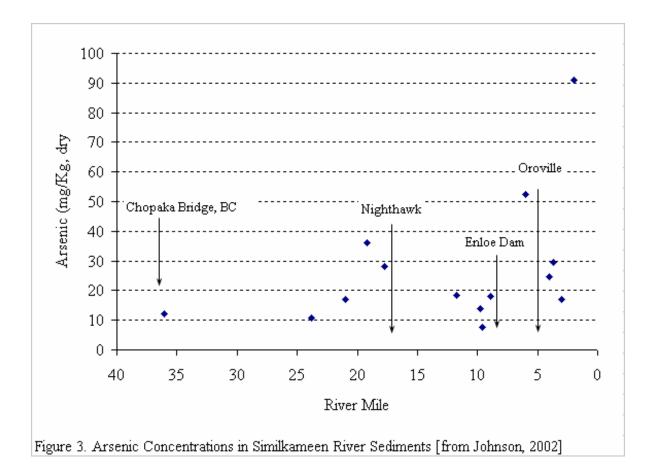
A typical, commercially available dredge is pictured in Figure 2

(http://www.keeneengineering.com/pamphlets/howdredge.html). The pictured dredge likely has a 4" diameter intake nozzle. These are the maximum allowed under authority of the *Gold and Fish* pamphlet and are typically used by small-scale prospectors and miners. Larger dredges can and have been permitted on the Similkameen River, and are typically used by miners operating on a commercial basis.



Figure 2. A Typical Gold Dredge

Except for arsenic, the level of chemical contamination (both metals and organics) in Similkameen River sediments is relatively low (Johnson and Plotnikoff, 2000; Colville Confederated Tribe, Unpublished Data). Arsenic concentrations generally range from 10-50 mg/Kg^{*} (Figure 3). Samples in the vicinity of Nighthawk and Oroville have exceeded a recently proposed Washington State sediment quality guideline of 20 mg/Kg for protection of aquatic life (Avocet Consulting, 2003). Most Washington rivers and streams have less than 10 mg/Kg arsenic in the sediments.

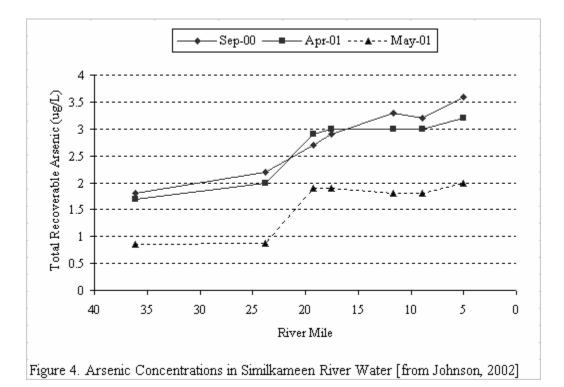


Arsenic is also elevated in the Similkameen water column, with concentrations of 1.0 - 5.0 ug/L^{**} typically being encountered (Johnson, 2002). The technical study conducted for the arsenic TMDL concluded that the major source of arsenic was tailings from historical mining activity in British Columbia (Johnson, 2002). Resuspension of contaminated sediments was identified as a potentially important source of arsenic to the water column. The arsenic concentrations in the Similkameen River exceed the federal human health criteria of 0.018 and 0.14 ug/L but are well within the state aquatic life criteria of 190 and 360 ug/L (see Table 1). The human health criteria are based on a one-in-one million excess cancer risk from consuming fish and water or fish only.

* parts per million

** parts per billion

In the absence of dredging, arsenic has previously been shown to increase slightly going downstream from Nighthawk to Oroville (Figure 4). The Palmer Lake outlet at r.m. 19.5 is a major source of arsenic to the lower river.



The previously mentioned dredging simulation study conducted by Ecology involved mixing predetermined amounts of river water and sediment to approximate a dredged material slurry (the Elutriate Test Described in Plumb (1981)). After shaking for 30-minutes, the supernatant from the mixture was allowed to settle, and then filtered and analyzed. The samples used in the test were obtained near Eagle Rock (r.m. 11.7) and just above Enloe Dam (r.m. 8.9), areas where dredging was either underway or planned. Arsenic concentrations were 14-18 mg/Kg in the bulk sediments and 3.9 ug/L in the river water.

Results of the simulation showed that arsenic, copper, lead, and zinc were the metals of primary interest. Arsenic concentrations in the elutriate were 5-10 times higher than the river water used for the test. Copper and lead exceeded aquatic life criteria by factors of 2-4. Zinc approached half its aquatic life criteria values. (There are no human health criteria for copper, lead, or zinc equivalent to the arsenic human health criteria.) A point source dilution model applied to these data suggested that at least a five-fold dilution would occur immediately downstream of a dredge during low flow conditions. It was concluded that water quality concerns were probably negligible for metals, at least with respect to individual dredges.

This coming August 18-21, the Resources Coalition will hold a rally on the Similkameen River (<u>http://www.inlinks.net/def2003.html</u>). The rally is being organized to allow the public to meet, participate, and learn about small-scale mining and prospecting by participating in these activities with miners. Representatives from regulatory agencies have been invited to attend. There is a current proposal to use up to three dredges with 8" diameter intake nozzles to operate closer than 200' from each other during the rally.

Project Description

In response to community and tribal concerns, Ecology concluded that a field study should be conducted to obtain water samples in the vicinity of small-scale dredges operating on the Similkameen River. The objectives of the study will be to determine if dredging: 1) exacerbates current exceedances of the human health standard for arsenic or 2) results in violations of the aquatic life standards for arsenic, copper, lead, or zinc.

Ecology will use these data to make an initial determination as to whether dredging activities are likely to cause a violation of water quality standards under the conditions observed. Results of the field study will be provided to regulatory agencies and the public. Given the variability inherent in a gold dredging operation and limited number of samples being collected for this study, the results should not be considered conclusive.

Three types of samples will be collected for the study: dredge effluents, dredge plumes, and ambient river water. Effluents will be sampled from fifteen dredges operating in different parts of the river. The turbidity plume downstream of three of the dredges will be sampled at selected distances to gauge the downstream extent of the impacted area. Finally, samples will be collected upstream of where the dredges are working to determine background concentrations for the metals of interest.

Clean sampling techniques and low-level analytical methods will be used to analyze arsenic, copper, lead, and zinc. Turbidity, total suspended solids (TSS), hardness, and pH will also be measured. Flow data will be obtained from the U.S. Geological Survey and Ecology gauging stations at Nighthawk and Oroville, respectively.

Field work will be conducted during July-September, 2004. The study will be conducted by the Ecology Environmental Assessment (EA) Program with field assistance provided by CRO. The samples will be analyzed by the Ecology Manchester Environmental Laboratory.

Organization, Schedule, and Cost Estimate

Organization

EAP Project Lead	Art Johnson, EAP (360-407-6766)
CRO Client/Field Assistance	Mark Peterschmidt (509-454-7843)
EAP Toxics Studies Unit Supervisor	Dale Norton (360-407-6765)
Manchester Environmental Laboratory Director	Stuart Magoon (360-871-8801)
Manchester Laboratory Inorganics Unit Supervisor	Dean Momohara (360-871-8808)
Ecology Quality Assurance Officer	Cliff Kirchmer (360-407-6455)
Ecology Environmental Information Management System	(EIM) data entry – Carolyn Lee

Schedule

July-September, 2004	Field work conducted and samples submitted to laboratory.
November 2004	Laboratory analyses completed and data reported to project lead.
February 2005	Draft report completed.
March 2005	EIM data entry completed.
March 2005	Final report completed.

Cost Estimate

The laboratory cost for this project is estimated at \$11,000 (50% discounted price at Manchester Laboratory; true cost is 2X).

Quality Objectives

The applicable water quality criteria for metals are shown in Table 1. For hardness-dependent criteria (copper, lead, and zinc) the lowest value recorded for the Similkameen River at Oroville was used to calculate the criterion (<u>http://www.ecy.wa.gov/programs/eap/flow/shu_main.html</u>). Criteria concentrations increase with increasing hardness.

Table 1. Applicable Water Quality Criteria for Metals (ug/L)

			Human Heal	th Criteria**
	Aquatic Li	ife Criteria*	Fish + Water	Fish
	Acute	Chronic	Consumption	Consumption
Arsenic	360	190	0.018	0.14
Copper	7.7	5.5		
Lead	25	0.99		
Zinc	56	51		

*dissolved metals at 43 mg/L hardness

**inorganic arsenic

The Class A turbidity criterion (173-201A WAC) also applies in this case and states that "Turbidity shall not exceed 5 NTU over background turbidity when the background turbidity is 50 NTU or less, or have more than a 10 percent increase in turbidity when the background is more than 50 NTU."

A performance based approach was followed for defining measurement quality objectives (MQOs) for this project (Table 2). The MQOs are Manchester Laboratory's acceptance and reporting limits for the analyses selected.

Parameter	Check Standards/ LCS (recovery)	Duplicate Samples (RPD*)	Matrix Spikes (recovery)	Matrix Spike Duplicates (RPD)	Required Reporting Limits
Arsenic	85-115%	20%	75-125%	20%	0.1 ug/L
Copper	85-115%	20%	75-125%	20%	0.1 ug/L
Lead	85-115%	20%	75-125%	20%	0.02 ug/L
Zinc	85-115%	20%	75-125%	20%	0.5 ug/L
Hardness	85-115%	20%	75-125%	20%	1 mg/L
TSS	80-120%	20%	N/A	N/A	1 mg/L
Turbidity	80-120%	20%	N/A	N/A	0.5 NTU

Table 2. Measurement Quality Objectives

*RPD = relative percent difference

Reporting limits this low are needed to quantify background metals concentrations in the Similkameen River. The metals reporting limits for this project are lower than the aquatic life criteria by more than an order of magnitude and should, therefore, easily suffice for identifying exceedances of metals standards. Because the Similkameen already substantially exceeds the human health criteria for arsenic, compliance is not a reporting limit issue. The 0.5 NTU reporting limit for turbidity is an order of magnitude below 5 NTU, sufficiently low to assess violations of the criterion.

Design of Field Study

The field study will occur during July through September, 2004. Monthly average river flow during this period ranges from 3,029 cfs (July) to 600 cfs (September).

Three field trips are planned. The first samples will be collected soon after the mineral prospecting work window through the *Gold and Fish* pamphlet opens on July 1. The second sample set will be collected during the Resources Coalition rally in August. A third set of samples will be collected during September low flow. CRO is coordinating the field work with rally organizers, participating miners, and WDFW.

Dredge Effluents

Dredging primarily occurs from a few miles above Nighthawk down to Oroville near the mouth of the river (see Figure 1). To the extent possible, the locations sampled will be selected to give results that represent this entire reach. Likely access points are r.m. 19, 14.5-16, 11.8, 9-10.5, and 4-5.5 (Mark Peterschmidt, CRO, Personal Communication). CRO is seeking permission to obtain samples from dredges that plan to operate in these areas. The discharges from up to15 dredges will be sampled, ideally three from each access point.

A single sample will be collected from each dredge at the point the discharge leaves the sluice box. For dredge operations where the plume is being sampled (see below) three effluent samples will be collected.

The effluent samples will be collected by filling a one-liter sample bottle in quarter-volume increments over a five-minute period, in an effort to obtain a representative time-dependent composite. The sample will be allowed to settle for 45 minutes and then ½ liter decanted into sample containers. This will remove sand and other large particles that would normally settle out of the water column. A settling time of 45 minutes was selected based on the settleable solids analysis in EPA Method 160.5.

The effluent samples will be analyzed for total recoverable arsenic, copper, lead, and zinc. By statute, a total recoverable analysis is required for metals point sources to account for the total amount being discharged to a waterbody.

Effluent flow rates will be estimated from the water velocity and dimensions of the sluice box, and pump specifications. These results, along with measurements of stream depth and velocity, channel width, river flow, and ambient metals partitioning, will be used in a point source dilution model to estimate water quality impacts under various dredging scenarios.

Dredge Plumes

The plumes from three dredges operating in under varying river flows--one each in July, August, and September--will be sampled to gauge the downstream extent of the impacted area. Three samples each will be collected at 10, 50, and 200 ft. below the dredge, staggered over

approximately a one-hour period. The dredge effluent will be sampled at the same time. A single sample will also be collected immediately upstream of the dredge suction hose for comparison with the plume. A marked poly line with a float at the far end will be attached to the back of the dredge to locate the downstream sampling points.

The upstream and plume samples will be analyzed for total recoverable arsenic; dissolved copper, lead, and zinc; TSS; turbidity; and hardness. Arsenic is being analyzed as total recoverable for comparison to the human health standards, which are based on inorganic arsenic. Most of the arsenic in the Similkameen River water is in inorganic form (Johnson, 2002). Measuring inorganic arsenic directly would be more expensive. Total recoverable arsenic can reasonably be compared to the dissolved aquatic life criteria, since they are little different from the total recoverable criteria on which they are based. Copper, lead, and zinc are being analyzed as dissolved for comparison with the aquatic life standards.

Ambient River

Additional samples will be collected in the Similkameen River near Nighthawk to measure background concentrations for the metals and other parameters of interest. These samples will be collected in the early morning to ensure that no dredges are operating upstream.

Three samples will be collected for each field trip and analyzed for total recoverable and dissolved arsenic, copper, lead and zinc; and also for turbidity, hardness, and pH. In addition to setting background conditions, the data will be used to determine how these metals apportion between particulate and dissolved fractions, information needed in the point source model mentioned above.

Number of Samples

The number and type of samples to be collected for this project are summarized in Table 3.

Table 3. Su	mmary of S	Samples to	be Collected
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Sample Type	No. of Sites	Samples per Site	Subtotal	Analyses
Dredge Effluent	15	1-3	21	TR As, Cu, Pb, Zn
Dredge Plume	3	10	30	TR As; Diss Cu, Pb, Zn; TSS; turb.; hard.
Ambient River	1	9	9	TR As; Diss Cu, Pb, Zn; TSS; turb.; hard.
" "	1	9	9	TR Cu, Pb, Zn
Filter Blanks	3	1	3	Diss As, Cu, Pb, Zn
		Total =	72	-

TR = total recoverable

Diss = dissolved

Sampling Methods

Table 4 lists the sample size, container, preservation, and holding time for each study parameter. Sample containers will be obtained from Manchester Laboratory.

Parameter	Minimum Quantity Required	Container	Preservative*	Holding Time
Metals	250 mL	500 mL Teflon bottle	HNO ₃ to pH<2, 4°C	6 months
Hardness	100 mL	125 mL poly bottle	H_2SO4 to pH<2, $4^{\circ}C$	6 months
TSS	1,000 mL	1,000 mL poly bottle	Cool to 4°C	7 days
Turbidity	100 mL	500 mL polyl bottle	Cool to 4°C	48 hours

Table 4. Sample Containers, Preservation, and Holding Times for Water Samples

*dissolved metals to be field filtered (0.45 micron)

Metals sampling procedures will follow the guidance in EPA Method 1669 *Sampling Ambient Water for Trace Metals at EPA Water Quality Levels*. All samples will be taken as simple grabs or grab composites.

Metals samples will be collected directly into pre-cleaned 500 mL (plume and ambient samples) or 1 L (effluent samples) Teflon bottles. The effluent samples will be allowed to settle and be decanted as previously described. Samples for dissolved metals will be filtered in the field through a pre-cleaned 0.45 um Nalgene filter unit (#450-0045, type S). The filtrate will be transferred to a new pre-cleaned 500 mL Teflon bottle. The whole water and filtered water samples will be preserved to pH <2 with sub-boiled 1:1 nitric acid, carried in small Teflon vials. Teflon sample bottles, Nalgene filters, and Teflon acid vials will be cleaned by Manchester, as described in Kammin et al. (1995), and sealed in plastic bags. Non-talc nitrile gloves will be worn by personnel filtering the samples. Filtering will be done in a glove box constructed of a PVC frame and polyethylene cover. pH will be measured with an Orion meter.

Field activities will be recorded in a bound notebook of waterproof paper. A hand-held GPS will be used to record sampling locations. All samples will be placed in polyethylene bags and held on ice for transport to Ecology Headquarters. All samples will be kept in a secure cooler and transported to Manchester Laboratory within one-to-two days of collection. Chain-of-custody procedures (Manchester Environmental Laboratory, 2003) will be followed.

Measurement Methods

Table 5 shows the number of samples, expected range of results, and analytical methods for this project. Metals will be analyzed by ICP/MS (EPA Method 200.8). Hardness will be analyzed by ICP (EPA Method 200.7), with Standard Methods 2340B algorithm used for the hardness calculation.

 Table 5. Laboratory Procedures

Analyte	Sample Matrix	Number of Samples	Expected Range of Results	Sample Prep Method	Analytical Method
Arsenic	whole water	60*	0.2- 500 ug/L	HNO ₃ /HCl digest	EPA 200.8
Copper	whole water	27*	0.5 - 500 ug/L	HNO ₃ /HCl digest	EPA 200.8
Lead	whole water	27*	<0.02 - 500 ug/L	HNO ₃ /HCl digest	EPA 200.8
Zinc	whole water	27*	<0.3 - 500 ug/L	HNO ₃ /HCl digest	EPA 200.8
Copper	filtered water	38**	0.5 - 50 ug/L	analyze directly	EPA 200.8
Lead	filtered water	38**	<0.02 - 10 ug/L	analyze directly	EPA 200.8
Zinc	filtered water	38**	<0.3 - 100 ug/L	analyze directly	EPA 200.8
Hardness	whole water	36	75 - 125 mg/L	N/A	EPA 200.7
TSS	whole water	36	1 - 200 mg/L	N/A	EPA 160.2
Turbidity	whole water	36	1 - 100 NTU	N/A	EPA 180.1

*analyzed as total recoverable

**analyzed as dissolved

Quality Control

Field and laboratory QC samples to be analyzed for this project are shown in Table 6.

	Field QC		Labora	tory QC	
Filter Parameter Blanks		Check Standards/ LCS	Method Blanks	Analytical Duplicates	Matrix Spikes
Metals	2	2/batch	1/batch	1/batch	2/batch
Hardness	N/A	1/batch	1/batch	1/batch	2/batch
TSS	N/A	1/batch	1/batch	1/batch	N/A
Turbidity	N/A	1/batch	1/batch	1/batch	N/A

 Table 6. QC Samples, Types, and Frequency (a batch is 20 unknowns)

Field Quality Control

One filter blank will be analyzed for each field trip to detect contamination arising from sample containers, the filtration procedure, preservative, or sample handling. The filter blanks will be prepared using the deionized water-filled Teflon bottles that Manchester provides for metals samples. For preparing the blanks, a bottle will be opened and filtered in the field, using the same procedure as for the river water samples. The filtrate will be transferred to a new bottle, after rinsing with a small amount of same filtrate, and acidified.

Field blanks will be prepared for metals only.

Analytical Quality Control

Laboratory QC samples will include check standards/laboratory control samples, method blanks, analytical duplicates, matrix spikes, and matrix spike duplicates, as indicated in Table 6.

Three metals samples will be analyzed in duplicate to provide estimates of analytical variability. The samples will be selected in the field as representing anticipated high, medium, and low metals concentrations. Samples for duplicate analysis will be identified on the sample tags and the chain-of-custody form. Duplicates for the conventional analyses will be selected by Manchester, following their standard practice.

The laboratory control samples (LCS) for the metals analysis will include SLRS-4 (Riverine Water Reference Material for Trace Metals, National Research Council Canada) or equivalent. SLRS-4 is certified for the low metals concentrations typical of ambient rivers and streams. Manchester will also prepare a spiked blank for the metals analysis. It will be spiked at 10-15 ppb. Manchester's data report will include the metals concentrations measured in the LCS samples and their names, sources, and certified values, in addition to the percent recovery data normally reported.

Manchester's analysis of SLRS-4 indicates it may be biased high for arsenic (Dean Momohara, Manchester Laboratory, Personal Communication). If the same discrepancy is observed for this project, Manchester's need not qualify the arsenic data.

Data Verification and Validation

The field notes will be verified by reviewing this information prior to leaving each sampling site.

Manchester will verify the laboratory data by examining their results for errors or omissions and examination of the QC results for compliance with acceptance criteria. Reviewers use EPA 540/R-94-013, U.S. *EPA Contract Laboratory Program National Functional Guidelines for Inorganic Data Review, February 1994.* Their findings will be documented in a case narrative.

The data package will be validated by the project lead who will use professional judgment to determine whether the procedures in the methods, SOPs, and Quality Assurance (QA) Project Plan were followed. Once the data have been verified and validated, the project lead will examine the data to determine if the MQOs have been met.

Data Analysis

The field and laboratory data will be entered into Excel spreadsheets. Hardness results will be used to calculate the water quality criteria corresponding to each sample, using the Ecology spreadsheet tsdcal11.xls (<u>http://www.ecy.wa.gov/programs/eap/pwspread/pwspread.html</u>), and exceedances identified.

The dredge plumes will be characterized with respect to downstream extent and exceedances of standards. A point source model (pwsspread.xls <u>http://www.ecy.wa.gov/programs/eap/pwspread/pwspread.html</u>) will be used to characterize dilution. EPA's SMPTOX3 program (<u>http://epa.gov/ceampubl/swater/smptox3/index.htm</u>) will be used to simulate the effects of different numbers and locations of dredges on metals concentrations in the river.

On, or before, March 2004, the project lead will prepare a draft report of findings. The report will include:

- maps of the study area showing sampling sites
- descriptions of field and laboratory methods
- a list of the dates, locations, and sizes of the dredges sampled
- discussion of data quality and the significance of any problems encountered in the analyses
- summary tables of the field and laboratory data
- results from the data analysis
- conclusions and recommendations with respect to the potential for small-scale gold dredging to exceed state water quality standards within the Similkameen River

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