Addendum to the Work Plan for Sandia Canyon and Cañada del Buey, Revision 1

Scope (New, modified, or ongoing activity)	Work Description	Rationale
Archival Work (ongoing)	A review of solid waste management units and areas of concern in Los Alamos, Sandia, and Mortandad canyons was conducted to identify the potential source(s) of chromium (including the mass associated with each source) as part of the "Interim Measures Investigation Report for Chromium Contamination in Groundwater" (LANL 2006, 094431). Additional review will further constrain the mass of chromium and volume of effluent released to these canyons. This review will also improve estimates of other contaminants released to Sandia Canyon, such as zinc, phosphate, molybdenum, and arsenic.	Knowledge of groundwater flow paths and operations at Los Alamos National Laboratory (LANL or the Laboratory) support a focus on Los Alamos, Sandia, and Mortandad canyons as the likely sources of chromium in the regional aquifer in and around R-11 and R-28. The likely sources are related to usage of chromate-containing compounds to inhibit corrosion in cooling-tower systems that discharged to each of the three watersheds. Lesser sources include electroplating and photo processing facilities. Information about sources and release histories will be incorporated into models evaluating fate and transport of chromium and other mobile constituents. Delineation of transport rates and flow paths within Sandia Canyon will be improved by tracking contaminants that were released concurrent with and following chromium releases. Model simulations will incorporate bounding estimates of released contaminant masses to quantify the level of resolution in mass estimates required to evaluate potential remedial options.
Sediment Investigation (modified)	The Laboratory proposes to modify the scope of the Sandia Canyon sediment investigation described in the work plan (LANL 1999, 064617) by (1) modifying the locations of Phase 1 investigation reaches, (2) modifying Phase 1 numbers of sample and analytical suites, adding supplemental analyses to evaluate chromium geochemistry, and (3) using field x-ray fluorescence (XRF) measurements to help in the selection of samples submitted for off-site analysis and to enhance the robustness of the nature and extent determination of chromium in sediments. These three actions are described below in detail: (1) The Laboratory proposes to add an additional upcanyon reach closer to the primary contaminant source ("S-3 West") and to eliminate two downcanyon reaches (S-4 Central and S-5 West) from the initial sampling phase. (2) The Laboratory proposes five changes to the Phase 1 sediment analyses, as presented in the work plan. First, chromium(VI),	The modification of the list of priority reaches specified in Table 7.1.2-1 of the work plan (LANL 1999, 064617, p. 7-9) will better focus work on evaluating the nature of chromium contamination. The new reach, S-3 West, will be roughly midway between reaches S-2 and S-3, in a portion of the canyon relatively close to the primary contaminant source that is expected to be important for understanding the chromium inventory in the Sandia watershed. The two reaches eliminated from this first phase of investigation, S-4 Central and S-5 West, are in an area of expected relatively low chromium contamination, based on sample data from reaches S-3 and S-5 Central collected in 2000. In addition, any contamination in S-4 Central and S-5 West will be adequately bounded by data from the nearby reaches, S-4 West, S-4 East, and S-5 Central. S-4 Central and S-5 West could be further investigated in later phases if such work is required. The modifications to the analyte suites and sample numbers will provide better Phase 1 characterization than presented in the work

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	molybdenum, isotopic thorium, perchlorate, polycyclic aromatic hydrocarbons, and volatile organic compounds will be added to the analytical suite in all full-suite samples. Second analyses in S-3 West will be restricted to chromium and other metals, chromium(VI), molybdenum, and polychlorinated biphenyls as key contaminants. Analyses in the remaining Phase 1 reaches would include the full suite specified in the work plan. Third, approximately 40 samples will be collected in the wetland (reach S-2) for chromium and other metals to define the total chromium inventory better. Chromium(VI) analyses would also be obtained from these samples. Fourth, additional analyses will be conducted on approximately 20 samples to help evaluate the geochemical stability of chromium species. In addition to total chromium, chromium(VI), and other metals, the analyses will include iron(II), manganese(IV), phosphorus, nitrate, sulfate, sulfide, and total organic and inorganic carbon. Five, analyze approximately eight samples of cattails in reach S-2 for metals to evaluate potential biologic uptake. (3) The Laboratory will use a hand-held Innov-X XRF instrument to obtain field measurements of chromium concentration in sediment deposits in each reach prior to sampling. Measurements will be made for each stratigraphic interval at each geomorphic characterization location (stream banks, hand-dug holes, or hand-auger holes). These measurements will be used to determine variations in chromium concentration between different geomorphic units, sediment facies (fine-grained or coarse-grained sediment), and depth intervals. The XRF measurements will be used to provide preliminary estimates of chromium inventory in each reach and will be used to guide sampling. Samples selected for off-site analysis will include the location in each reach with the highest chromium concentration and also a range in concentration to provide representative average concentrations. The manufacturer's instruction manual is attached to this revision (Attachment 1).	plan, including: potential identification of a larger number of chemicals of potential concern; a better estimate of the inventory of total chromium, chromium(VI), and other analytes in sediment in the Sandia watershed; an improved evaluation of the geochemical stability of chromium; and an evaluation of the uptake of chromium and other metals into plants in the Sandia wetland. The results of field XRF measurements will provide a more robust determination of the spatial variations in chromium concentration and will help ensure that the locations with highest chromium concentration in each reach are sampled. Sampling for off-site analyses based on the field XRF data will also provide improved estimates of average chromium concentration and total chromium inventory in each reach.
Water Balance Investigation (new)	This activity will constrain the location and amount of surface water and alluvial groundwater loss in the narrow bedrock-dominated portion of Sandia Canyon between surface-water gaging stations E123 and	Areas of surface-water and alluvial-groundwater loss probably coincide with those parts of the canyon floor that contributed recharge to deeper perched zones and to the regional aquifer during and after

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	E123.5. The infiltration investigation conducted as part of the "Interim Measures Work Plan for Chromium Contamination in Groundwater" (LANL 2006, 091987) will be expanded by installing one or two new temporary stream gages, as allowed by the topography. Together with discharge data from outfalls and flow data from existing stream gages, the new stream gages will allow division of upper Sandia Canyon into three or four stream segments, providing better delineation of the areas of surface-water loss. Streambed infiltration losses will be determined by comparing surface-water flow between gages.	the period of chromium release from the Technical Area 3 (TA-03) power plant. A water-balance investigation, reported in the "Interim Measures Investigation Report for Chromium Contamination in Groundwater" (LANL 2006, 094431), showed that approximately 35% of the current TA-03 effluent volume to upper Sandia Canyon is lost along the approximately 3.5-km (2.2-mi) reach of canyon between the Sandia wetland and temporary gage E123.5. Further refinement of the water-loss estimates along this portion of Sandia Canyon will identify vadose-zone pathways and potential entry points for historical chromium contamination into the regional aquifer. These data will be applied in models of groundwater flow and chromium transport. These data will also help constrain the nature and extent of chromium and other contaminants.
Surface Water and Groundwater Sampling (modified)	Analytical suites for ongoing sampling conducted in Sandia Canyon, as described in the Interim Facility Groundwater Monitoring Plan (IFGMP), will be modified by adding stable isotopes of chromium (δ^{53}Cr) at the proposed locations. An initial sampling round will be conducted to determine if isotopic variations in δ^{53}Cr occur along surface water and groundwater flow paths within the Sandia and Mortandad watersheds. Samples from some of these locations may be at or below the lower concentration limit necessary for accurate and precise chromium isotope measurement, and/or the presence of high levels of organic matter may interfere with chromate extraction and analysis (Heikoop 2007, 095189). Based on results from the first round of sampling, some of these locations may be eliminated from future rounds of sampling if they are not suitable for analysis by this technique. In addition, variations in δ^{53}Cr for the initial round of data will be evaluated to determine if isotopic fractionation from the reduction of chromium(VI) to chromium(III) occurs along the surface water and groundwater flow paths. If evidence for isotopic fractionation is present, sampling will be conducted for three more quarters in the Sandia watershed and as approved in the next IFGMP for Mortandad Canyon.	Water-quality (geochemical) data obtained from one or more sampling rounds provide information about the occurrence and distribution of contaminants in surface and groundwater in the Sandia and Mortandad watersheds. Chemical and isotopic data will fingerprint potential contaminant sources and improve geochemical and hydrologic-transport numerical models that quantify processes controlling fate and transport of chromium and other contaminants of relevance (arsenic, molybdenum, and zinc). Ultimately, these data support the evaluation of potential remedial options. Analysis of δ^{53}Cr should enhance the geochemical conceptual model for chromium, including quantitative evaluation of chemical-biochemical reduction of chromium(VI) to chromium(III), followed by adsorption of chromium(III) onto ferric (oxy)hydroxide and/or precipitation of insoluble $Cr(OH)_3$. Analytical results for δ^{53}Cr are anticipated to provide quantitative information on the fate and transport and the natural attenuation of chromium in surface water and groundwater environments at the Laboratory.

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	Following completion of first phase of the sediment investigation, further consideration will be made to evaluate the potential usefulness of conducting chromium isotope analyses directly on sediment samples collected during the second phase. Stable chromium isotopes are proposed for addition to the current monitoring suites at the following locations: <u>Sandia Canyon</u> Surface Water – E121, E122, adjacent to SCA-1, E123, at new temporary gage station, and at E123.5 Alluvial Groundwater – SCA-1, SCA-3, SCA-5 Intermediate Groundwater – SCI-1, R-12 (screens 1 and 2) Regional Groundwater – R-11, R-10, R-10a, and R-35(a and b) when online <u>Mortandad Canyon</u> Surface Water – E1FW, E1E, E200 Alluvial Groundwater – MCO-0.6, MCO-2, MCO-4.5, MCO-5, MCO-7.5 Intermediate Groundwater – MCOBT-4.4, MCOI-5, MCOI-6 Regional Groundwater – R-1, R-15, R-13, R-28, R-33, R-14, R-34	
Fate and Transport Modeling (new)	This activity includes the development of a site-scale groundwater-flow and contaminant-transport model that incorporates historic chromium sources in Sandia, Mortandad, and Los Alamos watersheds, and existing water-supply wells in the vicinity (PM-3 and O-4). The model will include the vadose zone and the regional aquifer and will be based on all available hydrogeological data and supporting information, including the distribution of chemicals such as molybdenum and phosphate that replaced the use of chromium. The model will include detailed documentation of key input parameters and conceptual models and address uncertainties in the model results. The Laboratory will engage NMED in incorporating aspects of the conceptual model and plausible ranges and distributions for model input parameters. At a minimum, conceptual models to be considered	Numerical models are useful tools for integrating available knowledge about the fate and transport of chromium. Combining a quantitative treatment of all uncertainties with calibration and weighting of results based on their agreement with chromium measurements provides a defensible approach to providing quantitative answers to key questions such as: (1) What is the nature and extent of chromium? (2) What is the uncertainty in the nature and extent of chromium? (3) Is the current monitoring-well network capable of intercepting all potential chromium pathways? (4) What is the long-term fate of chromium in the vadose zone and regional aquifer? (5) What is the most effective and efficient remedial option for chromium? (6) What additional characterization is necessary to reduce model uncertainty sufficient to allow the selection of a remedial option?

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	will include those recently suggested, such as (1) the fault system that crosses the wetland as a fast pathway for chromium transport; (2) a vadose zone pathway that includes down-dip lateral spreading of perched intermediate groundwater above perching horizons; and (3) spatial and temporal changes to infiltration in Sandia Canyon from past erosion of canyon-bottom alluvium. Model results will be compared to available monitoring data as well as to estimates of the total mass of chromium in the system. If necessary, simulation results will be weighted based on agreement between simulated and measured concentrations. The model results will include, but will not be limited to, maps showing the expected concentration of chromium, the probability that chromium concentrations exceed maximum contaminant levels, and chromium concentrations associated with confidence limits agreed upon by the Laboratory and NMED.	
R-28 Testing (new)	R-28 will be pumped for at least 30 hr at a constant rate of approximately 5 gal. per minute while water levels, chemical constituents, and other indicator parameters are measured. In addition, water levels will be monitored continuously in R-35(a and b), R-11, R-13, R-15, and R-8A during the test. The 30-hr test duration should produce water that is currently located outside the “zone of influence” of the potential residual drilling fluids. The Laboratory will work with NMED before the test to define a set of potential test responses, in terms of water levels, contaminant concentrations, and indicator parameters. These potential responses will be based on conceptual models of flow and transport such as one model assuming that the chromium concentrations are affected by drilling fluids and another model assuming they are not affected by drilling fluids. These hypothetical responses will seek to identify unique responses of each conceptual model and ensure test design and sampling protocols that can observe these unique responses.	This test will evaluate the effects of possible residual drilling fluid contamination on measured chromium concentrations, provide insight into the nature of the chromium plume, and provide information on aquifer parameters to be used in conceptual and numerical models of chromium fate and transport.

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	Water samples will be collected at R-28 before pumping and during pumping at the following frequency: every hour during zero to 12 hr; every 4 hr from 12 to 24 hr; and at 30 hr at the end of pumping. Field parameters, including oxidation-reduction potential, temperature, pH, turbidity, specific conductance, and dissolved oxygen, will be measured during pumping and sampling. For all samples collected, filtered waters will be analyzed for metals and anions (including perchlorate), and nonfiltered waters will be analyzed for metals, total organic carbon, acetone, and 2-proponal (isopropyl alcohol). In addition, at the 4- and 6-hr intervals, filtered water samples will be analyzed for stable isotopes of nitrogen, and nonfiltered waters will be analyzed for low-level tritium (using electrolytic enrichment at the University of Miami) and stable isotopes of oxygen and hydrogen. To evaluate chromium reduction by potential residual drilling fluids, stable isotopes of chromium will be analyzed in samples collected at 0, 2, 4, 8, 12, 18, 24, and 30 hr. A field implementation plan (FIP) will be prepared to describe the details of the test at R-28. The FIP will include details of the test and the waste management plan for the purge water.	
PM-3 Zonal Sampling (new)	The Los Alamos County Utilities Department informed the Laboratory that access to PM-3 will not be granted until at least the fall of 2007.	Zonal sampling may provide insights into depth-dependant variations in the quality of water entering the well screen at PM-3. The Laboratory proposes that the need for zonal sampling at PM-3 be assessed after results for the R-35 and numerical modeling activities are evaluated.
Vadose Zone Boreholes (new)	NMED requested that one to two vadose-zone characterization core holes be installed approximately a mile upstream of SCC-1, if accessible. Field visits indicate that there are no accessible sites close enough to the stream channel in this portion of the canyon for installing core holes.	Proposed fate and transport modeling studies can evaluate different infiltration scenarios for this part of the canyon. In addition, geochemical data provided by sediment and water samples collected from the Sandia wetland, surface water, alluvial groundwater, intermediate groundwater, and regional groundwater will support evaluation of chromium migration pathways. The need for additional deep core hole investigations will be evaluated in the context of numerical modeling results.

REFERENCES

Heikoop, J., January 11 and 25, 2007. Chromium Isotopes. Personal communication between J. Heikoop and T. Johnson, Los Alamos, New Mexico. (Heikoop 2007, 095189)

LANL (Los Alamos National Laboratory), September 1999. "Work Plan for Sandia Canyon and Cañada del Buey," Los Alamos National Laboratory document LA-UR-99-3610, Los Alamos, New Mexico. (LANL 1999, 064617)

LANL (Los Alamos National Laboratory), March 2006. "Interim Measures Work Plan for Chromium Contamination in Groundwater," Los Alamos National Laboratory document LA-UR-06-1961, Los Alamos, New Mexico. (LANL 2006, 091987)

LANL (Los Alamos National Laboratory), November 2006. "Interim Measures Investigation Report for Chromium Contamination in Groundwater," Los Alamos National Laboratory document LA-UR-06-8372, Los Alamos, New Mexico. (LANL 2006, 094431)