Final

SUMMARY REPORT:

2003 NPDES Outfall Monitoring

Barbara Hoditschek New Mexico Environment Department Department Of Energy Oversight Bureau

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Barbara Hoditschek, NMED-DOE/OB

PURPOSE:

The primary purpose of this effort was to assure that activities at the U. S. Department of Energy (DOE)/Los Alamos National Laboratory (LANL) are protective of public health and safety and the environment. Pursuant to an Agreement-In-Principle (AIP) between the State of New Mexico, the DOE, and the New Mexico Environment Department (NMED), the NMED-DOE Oversight Bureau (OB) was formed and funded by DOE to establish a comprehensive, coordinated, environmental oversight and monitoring program of LANL activities.

BACKGROUND:

DOE/LANL has held a National Pollutant Discharge Elimination System (NPDES) permit since June 1978. The current permit (NM0028355), issued by the administrative authority (Environmental Protection Agency (EPA) Region 6), became effective February 1, 2001. Pursuant to the permit, twenty-one (21) industrial and/or sanitary Outfalls (ATTACHMENT A) located throughout the DOE/LANL complex (FIGURE A) are regulated. Five (5) of the Outfalls listed in ATTACHMENT A are being petitioned by DOE/LANL for removal from the permit because they are no longer discharging.

LANL's Water Quality and Hydrology (WQH) - Group of the Risk Reduction and Environmental Stewardship (RRES) - Division is responsible for monitoring NPDES compliance and collecting grab and composite samples at NPDES outfalls. The NMED - Surface Water Quality Bureau (SWQB) is funded by EPA Region 6 to monitor NPDES permits issued in New Mexico.

METHODS:

OB staff is required to develop a Sampling Analysis Plan (SAP) before initiating sampling activities. A SAP (ATTACHMENT B) and Plan Addendum (ATTACHMENT AD), which outlined the monitoring activities designed to meet OB program objectives for oversight of the DOE/LANL NPDES permit, was written. Eight (8) of the sixteen (16) NPDES outfalls, which are known to regularly discharge to the environment, were selected for sampling during 2003. The Outfalls selected were: 02A129, 05A055, 13S, 03A048, 03A027, 03A181, 051 and 001. Scheduling for sampling of these outfalls was coordinated with the WQH - Group in advance. NMED-SWQB staff assigned to monitor the DOE/LANL NPDES permit was also invited to participate in the sampling activities.

ATTACHMENT C lists Outfall type and ID number, sampling dates, and analytical parameters and methods used for each outfall sampled. OB selected sampling parameters and EPA analytical methods listed in the NPDES permit for most of the outfalls sampled. Additional parameters and/or different analytical methods were also chosen (indicated in bold in **ATTACHMENT C**) by OB in order to evaluate EPA's decision in listing/not listing certain monitoring parameters in the permit. The decision to add perchlorate as an additional sampling parameter can be used to demonstrate the type of rationale use in the decision making process. Perchlorate is listed as a permit monitoring parameter in the permit, but for only three (3) Outfalls (051, 05A055 and 05A097). In addition, the monitoring requirement is as "report" only. Undoubtedly this decision was made by the regulatory authority because there currently is no State of New Mexico 20.6.4 NMAC "Standards for State or Interstate and Intrastate Surface Waters" (referred afterward in this report as "State Standards") standard for perchlorate. However, recent detection of low levels of perchlorate in ground-water wells located on or near Laboratory property by OB in 2003 prompted the decision to determine whether NPDES outfalls are possible corridors for transport of this contaminant.

While sampling the outfalls, LANL and OB staff observed operating procedures outlined in LANL's, *"Handbook for NPDES Compliance Sampling At Industrial Outfalls, Rev. 2."* "True" split samples were acquired at each outfall by using a churn splitter. The churn splitter, which was supplied by LANL, was operated according to procedures outlined in *USGS Technical Manual No. 78.03*. OB splits were submitted to OB contracted labs (Paragon, Pinnacle and/or Severn-Trent) and LANL splits were sent to a LANL contracted lab (GEL). All split - samples were non-filtered, kept on ice at 2 - 6^o C, and shipped via overnight carrier, or hand delivered to contract labs.

Field data (pH, and temperature) as well as Total Residual Chlorine (TRC) were taken during most sampling events. OB applied OB Standard Operation Procedures (SOPs) *IX. "Record Keeping"* (ATTACHMENT D (a)) and *VIII " Sample Preservation and Sampling"* (ATTACHMENT D (b)) as part of their sampling protocol.

OB staff also employed their SOP XI. "Quality Assurance/Quality Control" (ATTACHMENT D(c)) in reviewing their data derived from these sampling activities. In accordance with the OB Site-Specific Protocol (SSP, 1998), data sets were submitted to the Point-Of-Contact (POC) for the AIP program. The data sets, (contained on CDs), were distributed by the POC to DOE on May 5, 2003 and August 5, 2003 (ATTACHMENT E). Furthermore, a copy of this report will be submitted to the POC for distribution to DOE and LANL. Sampling results from RRES-WQH were sent to OB on April 15, 2003 (ATTACHMENT F).

RESULTS:

General Discussion:

ATTACHMENT G contains eight (8) Tables of analytical data obtained from the NPDES outfalls sampled. Outfalls are grouped in tables according to Permit effluent category (e.g. cooling towers, boiler blow-down). Data that exceed either NPDES or *"State Standards"* are discussed in this report. Temperature and pH data taken by either LANL staff and/or OB staff during each sampling event are also included on the tables. In addition, the tables also include TRC readings which were taken by LANL staff at Outfalls 03A048, 03A181, 03A129 and 001, and a sulfite (as $S0_3^{)-2}$ level taken from boiler blow down at Outfall 02A129.

Specific Comments:

Table 1: Outfalls 03A181, 03A027, and 03A048

Treated cooling water is discharged from these outfalls. Outfall 03A181 discharges to Mortandad Canyon, Outfall 03A027 to Sandia Canyon, and Outfall 03A048 to Los Alamos Canyon.

Parameters Evaluated: Arsenic, Molybdenum, Perchlorate, TSS, and Tritium.

Arsenic, tritium and TSS are compliance driven parameters routinely sampled for at all three of these outfalls. No exceedence of NPDES compliance values resulted in either the LANL or OB samples. In addition, no *"State Standard"* was exceeded in either sample set. All field parameters (pH, and temperature) and TRC taken at these outfalls were within NPDES limits

Although not listed as a permit parameter, **molybdenum** is a common component used in cooling tower descalers. Since cooling water is recycled in the cooling tower for a period of time before being discharged, the opportunity for molybdenum to concentrate may exist.

Perchlorate was not detected in the Outfall 03A027 split samples. Discharge water from this outfall has been run through cooling towers at the Supercomputing Complex (SCC) located at TA-3. The water source for these cooling towers is treated wastewater from the Sanitary Wastewater System (SWWS) located at TA-46 that has been transported cross canyon feed lines to a storage tank at TA-3. It is noteworthy that treated wastewater from the SWWS collected at Outfall 13S was non-detect for perchlorate.

Elevated levels of perchlorate were found, however, in the OB samples for Outfalls 03A048 (0.008 mg/l) and 03A181 (0.003 mg/L) while the LANL results were non-detect (ND) Since both OB and LANL sample sets were analyzed by Ion Chromatography (IC) using EPA Method DW1 *314.0 (from now on referred to as "Method 314")*, an explanation for the discrepancies between the sample results needed to be addressed.

Error in analytical data can originate from many sources; therefore, a holistic approach was taken in reviewing the data. Dissimilarity seen in the perchlorate values was discussed with LANL staff. LANL staff contacted their contract analytical lab and reported that the lab indicated they had applied a three-ionic-cartridge cleanup step recommended in *Method 314: Determination of Perchlorate in Drinking Water Using Ion Chromatography* (EPA, 1999) and suggested that this may be the source of the discrepancy between the two contract labs. OB discussions with their contract lab revealed this to be the case. The OB contract analytical lab indicated they had not applied the cleanup step. In addition, review of internal lab data associated with the samples indicated matrix interferences had occurred during the analyses.

Per OB's request, Outfalls 03A181 and 03A048 were resampled for the purpose of determining the cause of the matrix interferences observed by the OB contract lab while using *Method 314*. Also, as a backup evaluation, the OB contract lab agreed to apply the more sensitive, yet EPA unapproved Method 8321A for perchlorate.

The LANL contract lab again obtained no detects using Method *314* for perchlorate on the new samples obtained at Outfalls 03A181 and 03A048. The OB lab again obtained chromatograms with elevated baselines and multiple interfering peaks while using *Method 314*. The chromatograms for *Method 8321A*, however, did not show the same interference and peaks. In addition, all QC samples for *Method 8321A* were within control limits. The OB therefore accepted

and used the data generated by *Method 8321A* as a more accurate reflection of perchlorate concentration then Method 314 in this instance. *Method 8321A* data (0.001 mg/L) for both Outfalls 03A048 and 03A181 indicate perchlorate was present in these outfalls, but at a low level.

Evaluation of sludge associated with NPDES outfalls (e.g. from cooling towers) is not required by the NPDES permit. However, the problems experienced with the perchlorate analysis of the effluent from Outfalls 03A181 and 03A048 by the OB contract lab prompted this additional type of sampling. Cooling tower #53-963, (which is associated with Outfall 03A048), was chosen as the sludge source because it had recently been cleaned. The sludge sample was taken and split by LANL staff. LANL SOP, *"Procedures for Soil Sampling"*, was applied in collecting the sample.

ATTACHMENT H contains the analytical results of the cooling tower sludge. The sludge was analyzed for perchlorate, heavy metals, and gross alpha and beta. Data obtained for these parameters were compared to LANL sediment background values. Copper and zinc were the only parameters in both split samples whose results exceeded background values. Unfortunately, calculation of the relative percent difference (RPD) between the LANL and OB data revealed that the data were not comparable.

While sampling at Outfall 03A027, two observations of environmental conditions requiring attention, were made by LANL and OB staff. The first situation involved erosion control matting that had been placed at the sloped entrance to the walkway leading to the outfall (FIGURE B). The erosion control matting was so damaged that it had become a safety hazard. The damage may have been caused during a fire hydrant sediment removal procedure. During the flushing process, the fire hose used to drain the hydrant was probably placed directly on the erosion (jute) mat. The high pressure exerted by the hydrant water scoured out a deep hole below the jute mat and left the mats fine-stranded plastic mesh exposed. Since the exposed mesh was located directly in front of the path leading to Outfall 03A027, it posed a trip hazard for anyone needing to get to the outfall. LANL staff informed the facility operators associated with the outfall, and the site was eventually stabilized by filling in the hole and covering over the lose mesh with gravel (FIGURE C).

The second observation involved an unidentified 55-gallon barrel. The barrel was sitting on a pallet located next to the fence at the north side of a cooling tower near Outfall 03A027. It was open, unlabelled and contained sediment with vegetative growth. Since the barrel was unlabeled, it could not be established if the sediment it contained was sludge that had been removed from the cooling tower basin.

LANL staff contacted the appropriate facility operator concerning the barrel and was informed that the barrel was to have been removed last year to the landfill but must have been overlooked. The barrel apparently had been labeled, and someone had forgotten to replace the lid after the contents had dried. Since the contents had been analyzed and were found to be non-hazardous, the barrel was relabeled until final deposition at the Los Alamos County landfill.

Table 2: Outfall 001

Outfall 001 discharges power plant water to Sandia Canyon. Discharge from this outfall also contains treated effluent from the Sanitary Wastewater System (SWWS). As part of the Labratory's Water Conservation Project, treated effluent is transported through a cross-canyon collection system and held in a 500,000-gallon storage tank at TA-3 until it is recycled. Treated effluent that is not recycled is discharged through Outfall 001.

Parameters Evaluated:

Molybdenum, Nitrate-Nitrite, PCB (Total and Congener), Perchlorate, TSS, TRC and Mercury. There was no exceedance in either NPDES or *"State Standard"* reported for sample data from this Outfall.

A TRC value of 0.04 mg/L was obtained during the split sampling event of March 11, 2003. This result was higher than the 0.00 mg/L value routinely obtained at this site. The 0.04 mg/L value however, is less then the MQL for TRC (0.10 mg/L), therefore, a "zero" was reported on the monthly Discharge Monitoring Report (DMR). This is in compliance with language found in *"Part II"* of the NPDES permit stating, *"If any individual analytical test result is less than the minimum quantification level listed at Part II.A of this permit, a value of zero (0) may be used for the Discharge Monitoring Report (DMR) calculations and reporting requirements."*

Upon notification by WQH staff of the higher TRC value, power plant personnel increased the injection rate of chlorine neutralizer into the Outfall effluent. Power plant personnel also informed WQH staff that they were exploring the relationship between oxygen-reduction potential (ORP) and TRC. Their plan is to operationally monitor TRC concentration using the already installed ORP meter at the Outfall.

Because the MDL for the reagents the WQH used during the March sampling event at Outfall 001 was near the detection limit, WQH staff scrutinized the method and analytical kit they use to monitor for TRC. *HACH Method 8167* (N, N-diethyl - pphenylene diamine (DPD) colorimetric method) is used for each new batch of reagents to establish the MDL used in the TRC determination, and a *HACH DR820* colorimeter with *Accuvac* vials is used to perform the TRC analysis. The MDL for the current reagents used during the March sampling event at Outfall 001 was 0.022 mg/L.

The WQH staff also followed up on the TRC anomaly at Outfall 001 by contacting the manufacturer, HACH. Staff had noticed earlier in the month that reagent readings were near the MDL for the method being used and were concerned that this could possibly be due to some sort of interference. HACH representatives suggested the *Accuvac* vial contents could be interacting with sunlight. WQH staff adjusted their procedures by keeping the vials out of the sunlight as much as possible and by incorporating a field blank (*Millipore*-water) with each analysis. Follow-up TRC compliance sampling at Outfall 001on March 17, 2003 and April 24, 2003 resulted in values of 0.00 mg/L.

Table 3: Outfall 051

Radioactive Liquid Waste treated at the Radioactive Liquid Waste Facility (RLWTF) is discharged from this Outfall to Mortandad Canyon

Parameters Evaluated:

PCB (Total and Congener), Perchlorate, ²³⁸Pu, ^{239,240Pu}, 226Ra, ²²⁸Ra, ⁸⁹Sr, ⁹⁰Sr, ²⁴¹Am, TSS, and Tritium.

TSS, ²²⁶**Ra**, ²²⁸**Ra**, **tritium**, and **perchlorate** are NPDES parameters routinely sampled for at this outfall. Effluent samples for NPDES monitoring are collected from a sampling sink located in Room 116 of Building TA-50-1.

Compliance samples are taken at the sampling sink located in Room 116 of the RLWTF. The sampling line was cleared of air, line precipitants, etc. for 20-30 minutes. No discharge was being released to the canyon while this was occurring. Discharge released to the sink was recirculated and reprocessed. Sampling commenced when it was determined by facility staff that the lines had been cleared and discharge was being released to the canyon.

During the sampling event, OB staff noted that the sample being collected was discarded twice before a discharge sample was finally collected. RLWTP staff who were collecting the sample,

indicated they had determined that the discarded discharges were "off color" and thus "non representative". OB staff advised RLWTP staff that as long as the effluent being sampled was being discharged to the canyon, it was "representative." A copy of the comments made to RLWTP staff was also provided in written form to LANL (ATTACHMENT I).

Both LANL and OB split-sample results for the NPDES parameters (**TSS**, **Perchlorate**, ²²⁶**Ra**, ²²⁸**Ra and Tritium**) were within permit limits. Of the parameters which are not NPDES permit compliance driven (⁸⁹**Sr**, ⁹⁰**Sr**, **PCB**, ²⁴¹Am, ²³⁸Pu, and ^{239,240}Pu)- - and for which no "*State Standard*" apply, ⁸⁹Sr, ⁹⁰Sr and PCB had results, - which did not prompt concern.

Radionuclides evaluated in this sampling event are however, subject to requirements of DOE Order 5400.5 whose stated purpose is, "to establish standards and requirements for operations of the DOE and DOE contractors with respect to protection of members of the public and the environment against undue risk from radiation." Standards and limits for radionuclides are contained within the DOE Order 5400.5 as "Derived Concentration Guide (DCG)" values.

DCG values set limits of concentration for radionuclides in air or water that under conditions of continuous exposure for one year by one exposure mode that would result in an effective dose equivalent of 100 mrem or 0.1 rem. With regard to known mixtures of radionuclides (a situation that applies to the RLWTF), the sum of the ratios of the observed concentration of each radionuclide to its corresponding DCG must not exceed 1.0.

⁸⁹Sr, ⁹⁰Sr, tritium and ²²⁶Ra ²²⁸Ra values from the split samples taken by OB and WQH fell within DCG limits. Results for ^{239,240}Pu, and ²⁴¹Am, however, exceeded DCG guideline values. The DCG limit for ^{239,240}Pu and ²⁴¹Am is 30 pCi/L. The analytical results for ^{239,240}Pu were 33.2 pCi/L and 118 pCi/L for ²⁴¹Am.

The wastewater treatment at the RLWTF has improved dramatically since 1999. This improvement is due to the addition of ultra filtration and reverse osmosis treatment units to the RLWTF operations. Effluent water from the RLWTF is held in two "frac" tanks from which samples are taken for analyses. Sum of Ratio values of 1.0 have been reported for forty of the 42 months over the time span January 2000 through June 2003. The twelve-month, flow-weighted running average has been reported as less than 1.0 since October 2000.

The unusually high results obtained from the split samples collected by WQH and OB however, led to the discovery that the quality of the water discharged to Mortandad Canyon via the NPDES permitted Outfall had a higher gross alpha activity than the RLWTF effluent water stored and sampled in the "frac" tanks. As a result, in order to identify why water quality being discharged to the canyon was different than that from the "frac" tanks, facility operators began sampling the water actually being discharged to Mortandad Canyon. Over a several week period of time (early April and May 2003) facility operators conducted sampling of water being discharged to Mortandad Canyon.

After extensive testing of the effluent being discharged and facility operations, facility operators uncovered multiple problems. The primary trouble resided with the configuration of the existing radioactive liquid waste influent/effluent pumping manifold and associated piping. A leaking valve discovered in the influent/effluent pumping manifold was allowing non-processed influent radioactive liquid waste to leak into the treated effluent piping. Moreover, radioactivity was leaching from the 40-year old discharge piping into the discharge line running from the RLWTF to Mortandad Canyon.

In order to correct this situation, facility operators drew up plans to isolate the effluent from the influent by replacing the leaking pump in WM-2 with a new discharge pump. Also, a new sample pump and tubing to the Room 116 sample sink (NPDES current point of compliance) would be installed. In addition, the 40-year old discharge line running from the RLWF to Mortandad Canyon would be abandoned and the facility effluent discharge (Frac) tanks would be modified so

that discharge could be directed to a previously abandoned 3-inch diameter cross-country line. Furthermore, when the planned changes were complete, NPDES compliance sampling would be switched from the sink in Room 116 to the end of the discharge pipe located in Mortandad canyon. All proposed changes were documented and submitted to EPA Region 6 for approval (ATTACHMENT J). Sampling of Outfall 051 in Mortandad canyon has been delayed however due to health and safety concern associated with the location of the pipe in the canyon.

Modifications to the system were completed late summer 2003. Facility operators' sampled effluents being discharged to Mortandad Canyon after the modifications were completed. Samples from the effluent pipe in Mortandad Canyon for gross alpha were taken at timed intervals starting August 11, 13, 14, 18, 20, 26, 28 and September 2, 2003. Results of the sampling indicate that the condition of the water being discharged to Mortandad Canyon had improved due to the modifications. The data indicate however, that slightly elevated gross alpha concentrations still occur during the first 10 minutes of the discharge. This is most likely due to the leaching of radioactive material from mineral deposits and pipe corrosion products lining the inside of the 3-inch cross-county abandoned discharge line that was used to replace the 40-year old discharge line to Mortandad Canyon. To address this leaching problem, facility operators plan to drain, prior to discharge to canyon, the 220 gallons of effluent in the flooded portion of the discharge line back to the RLWTF influent tank.

Table 4: Outfall 05A055

Parameters Evaluated:

Beryllium, Chromium, Cyanide, HMX, Nitrate-Nitrite, Perchlorate, ²³⁸Pu, ^{239,240Pu}, RDX, TNT, TSS, ²³⁴U, ²³⁵U, ²³⁸U.

High explosive water generated at various high explosive process operations and from laboratories that conduct explosives research is treated at the High Explosives Waste Water Plant (HEWTF) located at TA-16. The Outfall discharges to a west-entering tributary, which drains into Canon de Valle.

Beryllium, TSS, chromium, TNT, RDX and perchlorate are parameters routinely sampled at the outfall to determine compliance with the NPDES permit. **HMX, nitrate-nitrite**, ²³⁸Pu, ^{239,240}Pu were additional parameters added by the OB. The OB and LANL sample data indicate no exceedance of NPDES or *"State Standard"* occurred for all of the parameters sampled.

The current NPDES permit requires *"reporting"* the perchlorate result from an annual grab sample. Since there currently is no *"State Standard"* for perchlorate, no compliance level has been defined in the NPDES permit. Perchlorate values obtained during the March 2003 split-sampling event and analyzed using Method 314 were elevated both LANL and OB split samples. The LANL contract lab obtained a value of 57.4 μ g/L and the OB contract lab's value was 58 μ g/L. The elevated levels of perchlorate found in Outfall 05A055 discharge resulted in the HEWTF suspending further discharges to the environment.

Since the first time Outfall 05A055 was sampled for perchlorate on November 2001, the HEWTF outfall discharged an effluent with a steady and erratic increase in perchlorate concentration. During 2002, various investigations were initiated to locate the source(s) of the perchlorate contaminated waste stream to the HEWTF (ATTACHMENT K). During this time, Laboratory management and DOE were also notified of the problem. A contaminated waste stream was eventually identified and administrative measures were taken to prevent further problems and proposals were made to install ion exchange units. However, no units were installed due to funding delays.

The elevated results for perchlorate obtained at the March 2003 split sampling at 05A055 alerted LANL staff that use of administrative controls to limit perchlorate in the waste stream to the HEWTF were not working. As a result, LANL revived the proposal to install ion exchange units to remove perchlorate at the HEWTF (ATTACHMENT L). Laboratory official identified two possible sources of the perchlorate contamination: residual perchlorate from the HEWTF's carbon filters that had come from previous treatment of wastewater from propellant-research; and from wastewater collected from a different facility that had rinsed perchlorate-contaminated equipment. The HEWTF discontinued discharging to the environment until the ion exchange units were installed in August 2003 (ATTACHMENT M).

Outfall 05A055 was resampled by LANL and OB staff on August 14. 2003. Analyses of the samples collected resulted in non-detects from both the LANL and DOE/OB contract laboratories.

Table 5: Outfall 13S

Treated effluent from the SWWS has never been discharged to Canada Del Buey. As part of LANL's Water Conservation Project, treated wastewater from SWWS is sent via cross-canyon lines to a storage tank at TA-3.

As of October 2003, effluent from the TA-3 storage tank is sent to the Sanitary Effluent Reuse Facility (SERF) were it is treated by microfiltration and reverse osmosis to remove silica. The RO product water, which is relatively corrosive, is then blended at a ratio of 2:1 with treated effluent water from the TA-3 storage tower, before it is made available to the cooling towers at the Supercomputing Complex at TA-3. Cooling tower blow down from the Supercomputing Complex is discharged through Outfall 03A027 to Sandia Canyon.

Unfortunately, treated TA-46 effluent has an elevated TDS (due to silica) and in order to comply with a NMED Ground Water Discharge Plan Standard for Total Dissolved Solids (TDS) and to prevent massive scaling problems for the cooling towers, the treated effluent is retreated. Additional treatment, which allows for recycling and reuse of TA-46 effluent, is provided –by the Sanitary Effluent Reuse Facility (SERF) located at TA 3. The effluent is retreated through a process of micro filtration to remove silica followed by reverse osmosis to reduce total dissolved solids (TDS). The facility, which began operating in October 2003, operates continuously.

Parameters Evaluated:

Aluminum, Antimony, Arsenic, Barium, Beryllium, Cadmium, Calcium, Chromium, Cobalt, Copper, Cyanide, Iron, Lead, Magnesium, Manganese, Mercury, Nickel, PCB (Total and Congener), Perchlorate, Potassium, Selenium, Silver, Sodium, Thallium, Tritium, TSS, Vanadium, and Zinc

Aluminum, arsenic, boron, chromium, cobalt, cadmium, copper, lead, mercury, selenium, tritium, TSS, vanadium, and zinc are parameters routinely sampled at this outfall to determine compliance with the NPDES permit. Sampling data indicate none of these parameters exceeded NPDES or *"State Standards"*.

Samples for this outfall are collected by plant personnel and transferred to LANL staff. Plant personnel had already taken the required TRC monthly sample, so a TRC analysis was not done. Review of past DMRs for this outfall revealed TRC values have been in compliance with NPDES requirements

Antimony, barium, beryllium, calcium, chromium, cyanide, iron, magnesium, manganese, mercury, nickel, PCB Total and Congener), perchlorate, potassium, silver, sodium, and thallium were also evaluated as additional parameters chosen by OB. None of these parameters exceeded "State Standards".

Table 6: Outfall 02A129

Discharge to this outfall consists of boiler-blow down and water-softener wastewater. Discharges are to Los Alamos Canyon.

Parameters Evaluated:

²⁴¹Am, Chromium, Molybdenum, Perchlorate, ²³⁸Pu, ^{239,240}Pu, Tritium, TSS and ²³⁴U, ²³⁵U, ²³⁸U.

TSS, chromium, and tritium are parameters monitored pursuant to the NPDES permit. ²⁴¹Am ^{239,240}Pu, ²³⁸Pu and ²³⁴U, ²³⁵U, ²³⁸U were evaluated because the Outfall is located at TA-21.

Radionuclides were included as sampling parameters although technical activities at TA-21 have ceased and its buildings are currently being dismantled. TA-21's historical involvement with uranium and plutonium (which would include ²⁴¹Am) dictated the choice of radionuclides sampled.

Perchlorate was included as a parameter to determine if low concentrations of perchlorate are concentrated to higher levels due to recycling of cooling tower water and/or water used in boilers. Perchlorate was not detected, and none of the parameters tested exceeded either NPDES or State water quality standards.

SUMMARY OF DATA REVIEW

General Overview

OB staff reviewed the data to determine variation between LANL and OB data results. Relative Percent Difference (RPD) was calculated for each outfall parameter sampled. RPDs were not calculated for parameters where one or both values was/were reported as "below detection limits" or "non-detect (ND)." RPD values can be found on each of the eight (8) tables (ATTACHMENT G).

OB staff applied the assumption that for a pair of results (for split samples sent to different laboratories to be analyzed for the same analytes), more than five to ten times the detection limit, the relative percent difference (RPD) between the two results should not be greater than 50% or further investigation is needed to determine the source of error. RPD values greater than 50% are indicated in bold print.

Significant differences in the split-sample analytical results for TSS, perchlorates, molybdenum, ²⁴¹Am, ²³⁸Pu, ^{239,240}Pu and sodium were found. This may be due to the overall measurement system or collection method used during sampling.

A churn splitter was used to obtain split samples. The reliability of obtaining a "true" split sample using this device had not been determine previous to commencing sampling. The churn splitter was designed to facilitate the withdrawal of a representative sub sample from a large composite sample of a waste-sediment mixture. They are designed to be used for compositing and sub sampling of chemical-quality samples that are to be analyzed for "total" or "total recoverable" inorganic constituents.

USGS Memorandum No. 78.03 has indicated there are limitations associated with churn splitter when collecting sample with relatively high concentrations of sand-size particles. This limitation was not a concern with the Outfall samples collected since all the samples came from processes where sand was not a factor. The USGS also indicates in the memorandum that it is important to churn the splitter at a rate of about 9 inches per second and that this is maintained during sample withdrawal. When faster or slower churning rates are used, maximum errors of about +/- -45 to +/- -65 % are common as compared with errors of about +/- -8 to +/- -15 % when using the 9 in/sec. rate. It is also important that the churn disc not break the water surface during mixing of the sample because this would aerate the sample and could cause chemical changes that would result in the sample no longer being representative of the water being collected.

At no time during the sampling events did the churn disc break the water surface, however, it cannot be verified that churning rate of 9 inches per second was maintained during all sampling events. Therefore, some of the variation seen between sample sets may be due to inconsistent of too slow churning rate. Future sampling events for split sampling NPDES Outfalls will include verification of the recommended churning rate.

For purposes of quality control checks of analytical methods, OB proposes to include at least one (1) field duplicate for each set of future samples collected at NPDES outfalls. LANL is required by the NPDES permit to verify the quality of field techniques and instrumentation by collecting duplicate samples on a minimum of 10% of samples collected.

Comments About Specific Parameters

TSS

At All Outfalls

In making error determinations regarding the two data sets, OB assumed that precision near the detection limit is often inherently poor due to instrument limitations; therefore, higher RPDs for TSS were not unexpected. The variation seen between the TSS datasets is consistent with observations made by USGS that indicated that the TSS method of analysis often results in unacceptably large errors. (e.g., *Collection and Use of Total Suspended Solids Data, Office of Water Quality and Surface Water, Technical Memorandum, USGS Policy 2000*).

Perchlorate

Outfalls 03A181 and 03A048

As discussed earlier in this report (discussion of Table 1, **ATTACHMENT G** results), the differences seen in the perchlorate results between the analytical labs used by WQH and OB have been resolved. The discrepancies originated from different applications of the same analytical method (Method 314). As a result of this discovery, the OB contract lab modified its application of Method 314, and WQH was made aware of the value of using Method (8321A).

Outfall 05A055

The discovery that elevated perchlorate levels were being released from this Outfall resulted in a quick and effective response (installation of ion filtration system) and public disclosure **(ATTACHMENT M)** from DOE. This is an excellent example of cooperation between LANL staff

and OB staff to bring about and improvement to the facility and the environment. If funding is available, OB will conduct at least one verification sample for perchlorate at this Outfall.

Sludge Evaluation for Perchlorate

Outfall 03A048

The primary intent of analyzing the cooling tower sludge as part of the 2003 NPDES sampling activity was to determine if perchlorate and/or any other cooling tower water constituents (e.g., components of descaling agents, heavy metals from cooling tower structures) could be concentrating in cooling tower sludge. A level of 0.008 mg/L of perchlorate had initially been detected in the effluent at this Outfall. Resampling of the effluent and application of a refined method for perchlorate detection (*Method 8321A*) by the OB contract lab resulted in a value of 0.001 mg/L. The WQH contract lab used Method 314 for both sampling events. Non-detects were reported for both events. Molybdenum values were not elevated, so it was not included as part of the heavy metal analytical parameter evaluation. *Method 314* and SW846 3050A/6020 were used to evaluate the sludge.

Sludge sampling results for Outfall 03A048 (ATTACHMENT H) are rounded to the nearest tenth. It is unfortunate that the data sets between the WQH and OB split samples of sludge from this Outfall were not comparable. This may be due in part to a matrix interference associated with the type of media being analyzed or to the fact that the OB sample labels were in error. The OB contract lab indicated on the Condition of Sample Receipt Form that the COC Agreement and Sample ID on the custody seal didn't match and that the labels were illegible (ATTACHMENT N).

Since the sludge data was inconclusive, re-sampling is recommended. In addition, with proper timing, several cooling towers could be sampled, thus, creating a broader database. The assumption that cooling tower sludge may concentrate constituents, that may leach out of the sludge and show up as elevated values in the effluent, is worthwhile pursuing.

TRC

Outfall 001

The problems experienced with TRC at this Outfall have been partially corrected. WQH has modified their sampling procedure to address possible interference. Although the facility operators did not pursue investigation of the relationship between ORP and TRC, they did install a second neutralizer pump as a backup if the first neutralizer pump fails again. Elevated TRC may however continue to be an issue at this Outfall.

Sodium

Outfall 13S

The data differences associated with the slightly elevated sodium values at Outfall 13S may be due to the Myox form of disinfectant being used at the treatment plant. The major constituent in this method of disinfection is sodium.

Molybdenum

All Cooling Tower Outfalls

Data indicate molybdenum is slightly elevated in treated effluent from cooling towers. Elevated levels of molybdenum at this Outfall may be indicative of concentrations of scale inhibitor components in the cooling tower sludge and/or tracer elements used by the facility. The 2004 sampling schedule will include the cooling tower Outfalls sampled in 2003 and eight additional cooling tower Outfalls. Molybdenum will be included as a sampling parameter for the 2004 sampling schedule.

Radionucluides

Outfall 051

As described in the narrative part of this report, the operational problems concerning Outfall 051 that triggered the high radionuclide concentrations in the WQH and OB split samples; have been addressed by the facility operators. OB however, is concerned that the facilities decision to connect the 40-year discharge line to the abandoned (TA-21) 3" discharge line may result in potential problems such as violation of DCGs goals due to sporadic releases of radionuclide constituents from scaling within the 40-year old pipe. The 40-year line is listed as RCRA Solid Waste Management Unit (SWMU) 50-006(d). Since it is now abandoned it will now need to be addressed by the RRES Group.

The abandoned (TA-21) 3" discharge line may also be a SWMU, and as such may not be suitable as a replacement for the 40-year discharge line. This matter will need to be discussed with the facility operators and appropriate RCRA management staff at both LANL and NMED.

Nevertheless, OB plans to reevaluate Outfall 051- OB staff will include in the Sampling and Analysis Plan (SAP) mention of the need to collect larger sample amounts so that any analytical interference that may occur during analysis at the contract labs, can be resolved. Sampling will again be conducted in conjunction with WQH staff and be collected at the end-of-the pipe during RLWTF scheduled discharges to Mortandad Canyon.

Recommendations For Future Sampling

The following recommendations are made based upon the observations and analytical results obtained during the 2003 sampling of eight NPDES Outfalls. In addition, in order to complete the evaluation of all currently permitted NPDES Outfalls, the remaining NPDES Outfalls not sampled in 2003 will be sampled in 2004. A draft of the Sampling and Analysis Plan is attached to this report (ATTACHMENT O).

Additional monitoring will be included in the 2004 NPDES Outfall Sampling Plan at Outfalls 03A048, 03A181 and 05A055 for perchlorate using both Methods 314 and 8321A. In addition the cooling tower sludge associated with these Outfalls as well as other cooling tower associated Outfalls will be sampled to establish baselines for heavy metals, perchlorate and possibly radionuclides. Outfall 03A181 will be reevaluated for molybdenum.

Outfall 13S will be reevaluated for sodium to determine if this parameter is elevated due to the type of disinfection currently being used at the facility.

The modifications recently made at TA-50 (new pumps and piping) and the impact of these modifications on the nature of the discharge from Outfall 051 will be evaluated.

The proposed 2004 NPDES Outfall Sampling and Analysis Plan (SAP) (ATTACHMENT O) addresses the issues discussed in this summary. Sampling will commence in April 2004 and continue through June 2004.

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EXECUTIVE SUMMARY

PURPOSE

The State of New Mexico - Deportment of Energy Oversight Bureau (NMED-DOE/OB) conducts sampling activities at the U. S. Department of Energy (DOE)/Los Alamos National Laboratory (LANL) to assure that activities at LANL are protective of public health and safety and the environment. In addition, OB monitoring determines DOE/LANL compliance with various permit requirements.

BACKGROUND

DOE/LANL has held an Environmental Protection Agency (EPA) Region 6 issued National Pollutant Discharge Elimination System (NPDES) permit since June 1978. The permit currently covers twenty-one (21) industrial and/or sanitary Outfalls. LANL's Water Quality and Hydrology (WQH) Group of the Risk Reduction and Environment Stewardship (RRES) and the NMED Surface Water Quality Bureau (SWQB) is responsible for monitoring activities associated with NPDES compliance.

The scarcity of monitoring activities at NPDES Outfalls by the State prompted OB to initiate sampling activities during 2003 at eight (8) Outfalls. The 2003 NPDES Outfall monitoring activities were funded by the National Nuclear Security Administration (NNSA).

RESULTS

For the most part, sampling results indicated that DOE/LANL was in compliance with their NPDES permit. However, several anomalies were discovered as a result of the sampling activity.

Perchlorate is a "report only" NPDES requirement and required at only three (3) of the 21 NPDES Outfalls. Perchlorate was found to be present at an elevated level at one of the Outfalls. Surprisingly perchlorate was also present at in low levels at two of the three cooling tower outfalls sampled.

LANL quickly resolved the problem at the Outfall with the elevated perchlorate by installing a filtration system to remove the perchlorate. OB is investigating the connection between perchlorate levels and cooling towers by sampling all NPDES permitted cooling towers and several cooling tower sludge during the 2004 NPDES Outfalls final round of sampling.

Elevated levels of several radionuclides in samples collected at the TA-50 Outfall prompted quick response from the facility. The cause of the elevated radionuclides was discovered and modifications to the facility were made. OB plans to verify the effectiveness of the modifications made by the facility operators and collect samples at a new, and more representative sampling location chosen by the facility during their 2004 NPDES Outfall sampling activities.

Several other beneficial effects which resulted because of the 2003 NPDES Outfall monitoring activity included: repair of massive erosion problems located above one of the Outfalls, refinement of a field parameter testing method for Total Residual Chlorine (TRC), instruction to facility operators on "representative" sampling, and the establishment of a cooperative and valuable rapport between the OB and WQH staff.

CONCLUSION

Although some problems were discovered as a result of this monitoring activity, the cost to DOE/LANL was minimal. The quick response by DOE/LANL to resolve the problem is invaluable in developing a positive public perception and demonstrating a responsible environmental stewardship.

Additional funding for the 2004 NPDES Outfall Sampling activity will be provided by NNSA.

LIST OF ATTACHMENTS

- A. List Of NPDES Permit # NM002835 Outfalls
- B. 2003 OB NPDES Outfall SAP
- AD. Addendum 1 To The 2003 OB NPDES Outfall SAP
 - C. OB 2003 Sampling Strategy For Eight (8) NPDES Outfalls
 - D. OB Standard Operation Procedures (SOPs):
 D (a) VIII. Sample Preservation/Sampling
 D (b) IX. Record Keeping
 D(c) XI. QA/QC
 - E. Copies of OB Letter Submitting 2003 NPDES Outfall Sampling Data
 - F. Copy of Letter from RRES-WQH Submitting NPDES Outfall Sampling Data
 - G. Eight Tables of OB and WQH 2003 NPDES Outfall Sampling Results
 - H. Table of OB AND WQH Analytical Results From Cooling Tower Sludge
 - I. Copy of OB Comments to WQH on TA-50 Sampling Procedure
 - J. Copy of Letter From WQH To EPA On TA-50 Modifications
 - K. List of LANL Investigations Conducted to Locate Perchlorate Contaminants
 - L. Copy of WQH Letter On HEWTF Modifications To Address Perchlorate
 - M. Copy of LANL News Release On The Discovery of Perchlorate At HEWTF
 - N. Copy of OB Contract Lab Comment on Condition Of Sample Receipt Form
 - O. Copy And Attachments For The OB 2004 NPDES Outfall SAP

LIST OF FIGURES

- A. Map Of Current NPDES Permitted Outfalls At LANL
- B. Photo Of Erosion Damage To BMP At Entrance To Outfall 03A027
- C. Photo Comparison Of Damage And Repairs To BMP At 03A027