Los Alamos
NATIONAL LABORATORY
EST. 1943

Environment, Safety, Health & Quality
P.O. Box 1663, K491
Los Alamos, New Mexico 87545
(505) 667-0666/FAX: (505) 667-5224

National Nuclear Security Administration
Los Alamos Site Office, A316
3747 West Jemez Road
Los Alamos, New Mexico 87545
(505) 667-5794/FAX (505) 667-5948

Date: February 23, 2011
Refer To: ENV-RCRA-11-0034
LAUR: 11-10030

Mr. Isaac Chen
U.S. Environmental Protection Agency, Region 6
Water Quality Protection Division
Permits and Technical Assistance Section (6WQ-PP)
1445 Ross Avenue, Suite 1200
Dallas, Texas 75202-2733

Dear Mr. Chen:

SUBJECT: LOS ALAMOS NATIONAL LABORATORY, NPDES PERMIT NO. NM0028355, SUPPLEMENTAL INFORMATION FOR NOTICE OF PLANNED CHANGE FOR THE ADDITION OF HARDNESS TO OUTFALL 051 EFFLUENT

Per your request, additional information is being provided regarding the Notice of Planned Change sent to the U. S. Environmental Protection Agency's Region 6 in December 2010 (reference ENV-RCRA-10-239) concerning plans to restore hardness to the Radioactive Liquid Waste Treatment Facility (RLWTF) effluent waters. The enclosed report is an evaluation of how hardness contributes to the whole effluent toxicity of Outfall 051 effluent. This report was prepared by Pacific EcoRisk in Fairfield, California (See Enclosure 1).

This information is provided as a follow-up to e-mail correspondence sent to you from Mike Saladen on December 23, 2010. Los Alamos National Security, Inc. (LANS) and National Nuclear Security Administration (NNSA) representatives will be scheduling a visit to your office in early March 2011 to continue this discussion.

Please contact Marc Bailey at (505) 665-8135 or Mike Saladen at (505) 665-6085 of the Water Quality and RCRA Group (ENV-RCRA) if you have questions or need additional information.

Sincerely,

Anthony R. Grieggs
Group Leader
Water Quality & RCRA Group (ENV-RCRA)
Los Alamos National Security, LLC

Sincerely,

Gene Turner
Environmental Permitting Manager
Environmental Projects Office
Los Alamos Site Office
National Nuclear Security Administration

ARG:GET:MB/lm

Enclosure: a/s

Cy: Brent Larsen, USEPA/Region 6, Dallas, TX, w/enc.
Mary Simmons, USEPA/Region 6, Dallas, TX, w/enc.
Glenn Saums, NMED/SWQB, Santa Fe, NM, w/enc.
William Olson, NMED/GWQB, Santa Fe, NM, w/enc.
Steve Yanicak, LASO-GOV, w/enc., M894
Michael Mallory, PADOPS, w/o enc., A102
J. Chris Cantwell, ADESHQ, w/o enc., K491
Hugh McGovern, TA-55-RLW, w/enc., E518
Pete Worland, TA-55-RLW, w/enc., E518
Mike Saladen, ENV-RCRA, w/enc., K490, (E-File)
Marc Bailey, ENV-RCRA, w/enc., K490, (E-File)
Bob Beers, ENV-RCRA, w/enc., K490, (E-File)
Randy Johnson, ENV-ES, w/enc., E500
Cindy Blackwell, LC-LESH, w/o enc., A187
ENV-RCRA, File, w/enc., K490
IRM-RMMSO, w/enc., A150

ENCLOSURE 1

An Evaluation of the Role of "Hardness" in the Amelioration and/or Exacerbation of Los Alamos National Laboratory Outfall 051 Effluent Toxicity

Prepared For:

Los Alamos National Laboratory
TA-3 SM-271 Drop Point 02U
Los Alamos, NM 87545

Prepared By:

Pacific EcoRisk
2250 Cordelia Road
Fairfield, CA 94534

February 2011
Report Revised February 23, 2011

PACIFIC ECORISK
ENVIRONMENTAL CONSULTING & TESTING

1. INTRODUCTION

The NPDES Permit No. NM0028355 issued to the National Nuclear Security Administration (NNSA) and Los Alamos National Security, LLC (LANS) for the Los Alamos National Laboratory (LANL) requires the permittee(s) to perform acute and/or chronic aquatic toxicity bioassays for several discharge outfalls throughout the Laboratory. Pacific EcoRisk, Inc. (PER) has been performing acute toxicity testing on LANL's Radioactive Liquid Waste Treatment Facility (RLWTF) Outfall 051 effluent using the freshwater crustacean *Daphnia pulex* since 2007. During this time sporadic occurrences of toxicity have been observed. Examination of the basic water quality characteristics of the 051 effluent suggests that the hardness of the effluent is playing a role in the observed toxicity.

1.1 Hardness in LANL Surface Water and Groundwater

Hardness is a natural component of water and is defined as the concentration of multivalent cations (mainly divalent cations). The primary hardness cations are generally calcium (Ca^{2+}) and magnesium (Mg^{2+}). The U.S. Geological Survey reports that some of the United States' hardest surface waters are found in New Mexico, Arizona, and Texas. Interestingly, while the Los Alamos region is surrounded by surface waters categorized as "very hard" (> 181 mg/L), it can be considered an "island" of surface water hardnesses typically in the "moderately hard"(60-120 mg/L) and "hard" (121-180 mg/L) range (http://water.usgs.gov/owq/hardness-alkalinity.html#map). This is consistent with the surface water hardnesses ranging from 52-159 mg/L that were measured for LANL ambient surface waters that were previously received and analyzed (Table 1) at the PER laboratory (PER 2005).

Table 1. Surface water quality characteristics of the Los Alamos ambient water samples.

Sample ID	Sample Date	Temp (°C)	pH	D.O. (mg/L)	Alkalinity (mg/L)	Hardness (mg/L)	Conductivity (µS/cm)	Total Ammonia (mg/L N)
CAMO-05-61170	7/26/05	10.8	7.72	10.7	119	111	357	<1.0
CAMO-05-61172	7/26/05	9.7	7.13	10.2	170	159	422	<1.0
CAMO-05-61174	7/26/05	7.9	7.24	11.3	138	117	423	<1.0
CAMO-05-61176	7/26/05	6.7	7.66	12.2	130	90	483	<1.0
CALA-05-61185	7/26/05	6.9	7.64	10.9	64	93	199	<1.0
CAMO-05-61166	8/18/05	6.0	7.05	10.2	90	99	244	<1.0
CAMO-05-61178	8/18/05	8.9	7.33	9.8	78	52	265	<1.0
CAMO-05-61180	8/18/05	8.9	7.80	11.1	92	82	271	<1.0

Data from PER 2005; water quality characteristics were measured at the time of sample log-in at the testing lab.

However, the source of water used at LANL is not surface water, but rather is domestic "tapwater" provided by Los Alamos County which pumps high-quality groundwater from the local aquifer via three water supply well fields (Otowi, Pajarito and Guaje), each of which has different hardness characteristics (Environmental Surveillance at Los Alamos during 2000, LA-13861-ENV):

- The Otowi field - The water hardness ranges from 63-89 mg/L (as $CaCO_3$);
  - calcium concentrations range from 20-22 mg/L;
  - magnesium concentrations range from 3-8 mg/L;
- The Pajarito field – The water hardness ranges from 42-96 mg/L;
  - calcium concentrations range from 11-27 mg/L;
  - magnesium concentrations range from 3-8 mg/L;
- The Guaje field - The water hardness ranges from 29 to 56 mg/L;
  - calcium concentrations range from 11-17 mg/L;
  - magnesium concentrations range from 1-3 mg/L.

Note -- Due to the unique hydrogeology of the aquifer that serves Los Alamos, its water hardness is comprised almost completely by calcium and magnesium.

This "tapwater" is used in LANL's radiological and nuclear facilities in a variety of applications. Wastewater from these facilities is collected and routed via a collection system to the influent tank at the RLWTF for treatment. Wastewater fed from this influent tank to the RLWTF treatment process is termed "RAW" influent. The treated water discharged from the RLWTF treatment process is termed "FINAL" effluent. The "RAW" influent to the RLWTF starts out with a hardness of approximately 40-45 mg/L (Table 2). However, the RLWTF's various wastewater treatment processes have the indirect effect of reducing the hardness in the Outfall 051 "FINAL" effluent to approximately 1-3 mg/L (range = 0.2-12 mg/L in 2008-09).

Table 2. Hardness-related water quality characteristics in LANL "Tapwater", "RAW" RLWTF influent, and Outfall 051 "FINAL" effluent

Water Quality Parameter	1994-1997[a]	2008[b]		2009[b]	
	"Tapwater"	"RAW" Influent	"FINAL" Effluent	"RAW" Influent	"FINAL" Effluent
Hardness (mg/L as $CaCO_3$)	48.9	41.8	1.47	44.6	2.7
Calcium (mg/L)	13	11.4	0.31	12.0	0.40
Magnesium (mg/L)	4	3.2	0.17	3.6	0.41

a - A Mathematical Model (AMIGA) of Solution Chemistry and Silica Solubility in High Silica Water at LANL, V. P. Worland, May 1997.

b - Data from 2008 and 2009 Annual Reports for the LANL Rad Liquid Waste Treatment Facility.

1.2 Importance of Hardness Ca^{2+} and Mg^{2+} Ions in Biological Systems

While the RLWTF's wastewater treatment processes effectively reduce the concentrations of many effluent contaminants (e.g., metals, etc.), the concomitant reduction of Ca^{2+} and Mg^{2+} concentrations could be problematic in that all organisms (i.e., plants, invertebrates, and vertebrates) require Ca^{2+} and Mg^{2+} in order to exist. These two elements are considered "the most important and abundant dissolved solids in freshwater" (Rand et al., 1995). There are numerous critical biological processes that are dependent on Ca^{2+} in order to function. It is essential for metabolic processes in all living organisms (Goldman and Horne 1983), a regulator of cell permeability (Ricklefs 1979), the main skeletal component of many animals and some plants (Goldman and Horne 1983). Ca^{2+} release is the trigger for many cellular events including muscle contraction (Lehninger et al., 1993). Mg^{2+}, which has a similar water chemistry to Ca^{2+}, is vital for energy transfer in every cell since it catalyzes the change from ATP to ADP (Goldman and Horne 1983). Plants also require Mg^{2+} to form the active center of the primary photosynthetic pigment, chlorophyll *a* (Goldman and Horne 1983).

A summary of the biological functions of calcium and magnesium is presented in Table 3.

Table 3: Roles of calcium and magnesium in critical biological functions

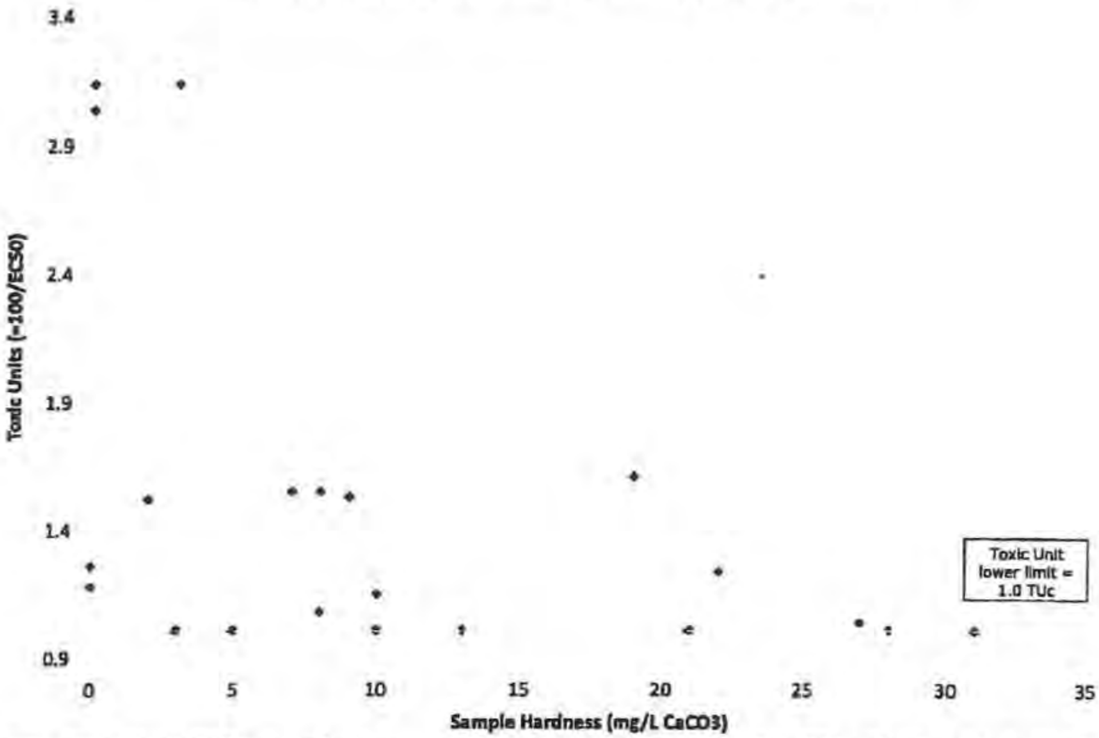
Micronutrient	Biological Function
Calcium (Ca^{2+})	Regulator of cell permeability Structural component of bone and skeletal structures Antagonistic influence on the uptake of metals Essential for metabolic processes in all living organisms Controlling factor in muscle contraction
Magnesium (Mg^{2+})	Structural component of chlorophyll Involved in function of many enzymes Vital for cell metabolism as the catalyst for transformation of ATP to ADP.

1.3 Low Hardness and Toxicity of RLWTF Outfall 051 Effluent

The roles of calcium and magnesium as essential to organism health appears to be reflected in the results of the 24 acute toxicity tests of the Outfall 051 effluent that PER has performed since 2007: when hardness levels are extremely low, there is generally an increase in the apparent toxicity of the effluent, and when hardness levels are >25 mg/L, virtually no toxicity is observed (Table 4 and Figure 1).

While there seems to be a correlation between extreme low hardness levels and increased toxicity, it is difficult to ascribe that completely to calcium and magnesium deficiencies. While the essential role for Ca^{2+} and Mg^{2+} in organism health is well known, few studies on adverse effects of extreme low hardness on aquatic organisms, and particularly daphnids, have been reported. Cowgill and Milazzo (1991) reported that daphnid (*Daphnia magna* and *Ceriodaphnia dubia*) reproduction declined below hardness levels of 72 mg/L, with 'total number of offspring' EC_{50}'s of 5 mg/L and 38 mg/L, respectively (in this context, EC_{50} is the hardness concentration predicted to have a 50% effect on the organisms). Cowgill and Milazzo also reported that *C. dubia* exhibited signs of stress when water hardness was below 9 mg/L.

Figure 1. Effects of Outfall 051 Hardness on Acute Toxicity



Note – Toxic Units (TU) are standard measures of the magnitude of toxicity, where TU > 1 indicates the presence of toxicity, with the magnitude of the toxicity increasing as the TU increases.

Lasier et al. (2006) similarly reported that *C. dubia* cultured in higher hardness waters (~100 mg/L) suffered reduced reproduction when exposed to low-hardness waters (40-50 mg/L); no such effects were observed for low-hardness organisms transferred to high-hardness waters. This suggests that the low hardness of the Outfall 051 effluent could cause adverse effects as it dilutes and lowers the hardness of any downstream ambient waters.

The Outfall 051 effluent is discharged into the Mortandad Canyon "receiving water", which is an ephemeral stream. Generally, the effluent infiltrates below the ground surface within 100 yards downstream of the outfall, although it may reach as far as 1-2 miles downstream before complete infiltration following significant storm events. However, as a precautionary 'worst case scenario' approach, it is responsible to be protective of the downstream aquatic ecosystems that do have established populations of aquatic organisms. The scientific studies cited above suggest that the reduction (and in some cases complete removal) of the hardness that is present in the "tapwater" and "RAW" influent to the low levels observed for the Outfall 051 effluent (and hence, in ambient waters downstream of the Outfall 051 effluent discharge) could directly or indirectly affect downstream receiving waters.

Table 4: Hardness levels and acute toxicity of LANL Outfall 051 samples (2007-2010)				
Sample Collection Date	Sample Hardness (mg/L $CaCO_3$)	NOEC (% Effluent)	EC_{50} (% Effluent)	Toxic Units ($100/EC_{50}$)
1/23/07	5	100	>100	<1
9/27/07	9	56	65.9	1.52
10/30/07	8	56	65.0	1.54
12/12/07	2	56	66.2	1.51
12/19/07	19	56	62.4	1.60
2/25/08	27	100	96.7	1.03
6/25/08	8	75	93.4	1.07
8/6/08	3	100	>100	<1
11/17/08	7	56	64.8	1.54
2/10/09	10	100	>100	<1
4/16/09	13	100	>100	<1
7/9/09	22	75	77.7	1.23
7/28/09	31	100	>100	<1
12/1/09	0	<32[a]	<32[a]	>3.13
1/4/10	0	<32	33	1.33
1/11/10	0	75	79.7	1.25
1/25/10	0	75	85.5	1.17
3/8/10	28	100	>100	<1
3/22/10	10	75	87.6	1.14
4/26/10	3	<32[a]	<32[a]	>3.13
6/8/10	21	100	>100	<1
7/12/10	0	<32	<32	>3.13
7/19/10	0	<32[a]	<32[a]	>3.13
11/18/10	31	100	>100	<1

a – There was complete mortality at all effluent concentrations.

Based upon this information, it is recommended that the hardness of the Outfall 051 effluent be restored to the hardness levels originally present in the "RAW" water prior to discharge. It is worth noting that this is recognized by regulatory agencies in their own guidelines for the performance of Toxicity Identification Evaluations (TIEs): California regulatory guidelines state that after performing ion-exchange treatment, "essential" ions Ca^{2+} and Mg^{2+} be added back to the effluent (Connor and Deanovic 1991).

1.4 Interaction Between Hardness and Contaminant Toxicity

The scientific literature clearly indicates the essentiality of Ca^{2+} and Mg^{2+} in ambient waters in order to maintain the health of aquatic organisms. The observation of toxicity at extreme low hardness levels may also be due in part to the general antagonistic effect of hardness (and particularly Ca^{2+}) on the toxicity of contaminants, and metals in particular. For instance, numerous studies have reported that hardness is protective of metals toxicity to the Outfall 051 test organism *Daphnia pulex* (or to closely-related *Daphnia magna)*, typically with Ca^{2+} having a greater protective effect than Mg^{2+} (Santore et al. 2001; deSchampheleare and Janssen 2002; Heijerick et al., 2002; Naddy et al. 2002; Kozlova et al. 2008; Clifford and McGeer 2009, 2010). In fact, the protective effect of hardness on metals toxicity to a wide variety of aquatic organisms is so well established that contemporary water quality criteria for metals generally are normalized to hardness levels of waters.

Again, the restoration of the hardness levels to the LANL effluent is recommended as a protective measure against potential contaminant toxicity to downstream aquatic organisms and to the *Daphnia pulex* organisms used in the acute toxicity tests of the Outfall 051 effluent.

2. SUMMARY AND CONCLUSIONS

The water used at LANL is a groundwater and has a hardness that is typically ~40-50 mg/L. However, after application of the various wastewater treatment processes at the RLWTF, the hardness of the Outfall 051 effluent has been reduced to levels as low as ~1 mg/L (the annual mean concentrations were approximately 1-3 mg/L, and ranged from 0.2-12 mg/L in 2008-09). This extreme low hardness is of potential concern as the hardness ions Ca^{2+} and Mg^{2+} are essential to maintain the health of aquatic organisms.

The reduction of the concentrations of these essential ions may be reflected in the observation of sporadic acute toxicity of the Outfall 051 effluent, particularly when the hardness is reduced to extremely low levels (e.g., to non-measurable concentrations). In addition, it can be expected that if present, the toxicity of contaminants, and in particular metals such as copper and zinc, will be increased at the extremely low hardness levels.

On that basis, it is highly recommended that LANL consider implementation of measures to restore the hardness of the effluent to the original source water levels. This restoration of hardness is also supported by the fact that regulatory agency guidelines similarly call for the restoration of water hardness levels to those concentrations existing prior to the application of treatment processes that remove Ca^{2+} and Mg^{2+}. In the interim, it is recommended that the effluent samples used for acute toxicity testing with *D. pulex* be amended with the hardness ions Ca^{2+} and Mg^{2+} to restore the hardness to the original "RAW" influent conditions.

3. REFERENCES

Clifford M, McGeer JC (2009) Development of a biotic ligand model for the acute toxicity of zinc to *Daphnia pulex* in soft waters. Aquatic Toxicology 91(1):26-32.

Clifford M, McGeer JC (2010) Development of a biotic ligand model to predict the acute toxicity of cadmium to *Daphnia pulex*. Aquatic Toxicology 98(1):1-7.

Connor V, Deanovic L (1991) A Laboratory Manual for the Preparation and Use of Ion Exchange Resins to Determine the Concentration and Biotoxicity of Dissolved Trace Metals in Freshwater Samples. Central Valley Regional Water Quality Control Board, Sacramento, CA.

Cowgill UM, Milazzo DP (1991) The sensitivity of two cladocerans to water quality variables: Salinity <467 mg NaCl/L and hardness <200 mg $CaCO_3$/L. Archives of Environmental Contamination and Toxicology 21:218-223.

Davies PH (1995) Factors Controlling Nonpoint Source Impacts. Pages 53-64 in: Herricks EE Jenkins JR (eds) *Stormwater Runoff and Receiving Systems: Impact Monitoring and Assessment*. CRC Press, Inc. Lewis Publishers, Boca Raton, FL.

deSchampheleare KAC, Janssen CR (2002) A biotic ligand model predicting acute copper toxicity to *Daphnia magna*: The effects of calcium, magnesium, sodium, potassium, and pH. Environmental Science and technology 36(1):48-54.

Goldman CR, Horne AJ (1983) *Limnology*. McGraw-Hill, Inc., New York, NY.

Heijerick DG, deSchampheleare KAC, Janssen CR (2002) Predicting acute zinc toxicity for daphnia magna as a function of key water chemistry characteristics: Development and validation of a biotic ligand model. Environmental Toxicology and Chemistry 21(6):1309-1315.

Kozlova T, Wood CM, McGeer JC (2008) The effect of water chemistry on the acute toxicity of nickel to the cladoceran *Daphnia pulex* and the development of a biotic ligand model. Aquatic Toxicology 91(3):221-228.

Lasier PJ, Winger PV, Hardin IR (2006) Effects of hardness and alkalinity in culture and test waters on reproduction of *Ceriodaphnia dubia*. Environmental Toxicology and Chemistry 25(10):2781-2786.

Lehninger AL, Nelson DL, Cox MM (1993) *Principles of Biochemistry: Second Edition*. Worth Publishers, Inc. New York, NY.

Mayer Jr FL, Marking LL, Bills TD, Howe GE (1994) Physiochemical factors Affecting Toxicity in Freshwater: Hardness, pH and Temperature. Pages 5-22 in: Hamelink JL, Landrum PF, Bergman HL, Benson WH (eds) *Bioavailability: Physical, Chemical and Biological Interactions*. CRC Press, Inc., Lewis Publishers, Boca Raton, FL.

Naddy RB, Stubblefield WA, May JR, Tucker SA, Hockett JR (2002) The effect of calcium and magnesium ratios on the toxicity of copper to five aquatic species in freshwater. Environmental Toxicology and Chemistry 21(2):347-352.

PER (2005) An Evaluation of the Toxicity of Los Alamos National Laboratory Ambient Waters to *Selenastrum capricornutum*. Report prepared for LANL. Pacific EcoRisk, Fairfield, CA.

Rand GM, Wells PG, McCarty LS (1995) Introduction to Aquatic Toxicology. Pages 3-66 in: Rand GM (ed) *Fundamentals of Aquatic Toxicology: Effects, Environmental Fate, and Risk Assessment, Second Edition*. Taylor and Francis, Bristol, PA.

Ricklefs RE (1979) *Ecology*. Chiron Press, Inc., New York, NY.

Santore RC, DiToro DM, Paquin PR, Allen HE, Meyer JS (2001) Biotic ligand model of the acute toxicity of metals. 2. Application to acute copper toxicity in freshwater fish and *Daphnia*. Environmental Toxicology and Chemistry 20(10):2397-2402.