# PALOS VERDES LANDFILL REMEDIAL INVESTIGATION REPORT

#### APPENDIX E.5

### MINERAL LEACHING STUDY; EXPERIMENTAL PROTOCOL

#### PALOS VERDES LANDFILL DPRIR MINERAL LEACHING STUDY EXPERIMENTAL PROTOCOL

<u>Project Description</u>: This study was initiated in an effort to help establish the range of background groundwater quality conditions present at Districts' landfills. The study includes laboratory experiments in which soil and bedrock samples from selected locations at each landfill were placed in contact with deionized water for a period of four to twelve months (perhaps longer) in order to see how many of the constituents in the soil/bedrock samples will solubilize. This experimental information will be used to supplement any field monitoring data from upgradient or background locations at a given landfill in order to try and establish background or baseline conditions at the landfill. A comparison of these background conditions with monitoring results from downgradient monitoring wells can help to establish whether or not contamination is present at these downgradient locations (and the degree of contamination, if present).

Field monitoring data from available background monitoring locations are the most appropriate information source for providing "composite" background water quality information for the site. By contrast, the experimental results are not as well suited to provide this kind of "composite" information, but the experimental results can be used to supplement or support similar information from field sources. The real strength of the experimental studies, however, is their ability to represent a wide variety of naturally occurring local extreme conditions for the site. Field monitoring data can not normally provide this information due to economic or physical limitations (i.e. wells can not be installed at sufficiently numerous locations to isolate all extreme conditions at some sites). Utilizing each of these sources of information together (field and experimental) to support each other rather than depending on either source standing alone seems like a more appropriate approach to use for this study. Indeed, an effort will be made throughout this study to use both sources of information in conjunction whenever possible (field data for indications of composite background conditions and experimental data to establish possible local extreme background conditions).

In the paragraphs below, a short discussion is presented demonstrating the experimental procedures used to conduct the laboratory studies.

<u>Soil and Bedrock Sample Processing</u>: The samples used for this study were core samples collected during installation of RI/FS borings at background locations. The core material was processed as follows:

- Available boring logs were reviewed and the cores inspected by a staff geologist
- Cores were sorted and grouped as required to produce reactors representative of discrete site conditions, including extreme conditions, while also grouping the samples so that reactor volumes (i.e. mass of material added) were sufficient to monitor (see later discussion for "Reactor Sampling").
- After sorting, the material was placed in one or two 12 qt. HDPE¹ tubs and sealed with an airtight lid. The amount of material added to the tub was recorded in the log book and was noted on the lid and side of the tub as follows:

<sup>1</sup> HDPE = high-density polyethylene

Reactor Number (e.g. "CA-101")
Sample Description (Barrier 4, bedrock)
Well Number, Depth, and Cumulative Mass (in grams)

- The material in the tub was processed as needed to homogenize the samples (since material from different wells and piezometers was placed into the same tub for some reactors) and to reduce the size of some of the larger particles in the samples (i.e. to expose more surface area to leaching). Processing included breaking up some of the "large" chunks of material by grinding them in a clean mortar and pestle (mortar and pestle were cleaned after each use with a 1% HNO<sub>3</sub> solution followed by a DI water rinse). After grinding a given portion of the sample, the crushed portion of the sample was placed back in the tub.
- Some of the material in the PVLF samples was too hard to grind by hand (in some cases it was only one or two small cores (2 inch diameter cores)). These hard samples were sent to an outside materials processing laboratory for mechanical grinding.
- After mixing the sample as much as possible, representative portions of the material were collected and stored in three 125 mL plastic bottles as needed for analysis (percent moisture and alpha and beta emissions) or for future inspection and/or research.
- The lid of the tub was resealed, the tub weighed (with mass recorded in log book as before), and the sample placed aside until needed later during reactor set-up (see next section).

Reactor Set-up: The reactors used for this study were assembled by placing soil/bedrock samples and deionized water into a 5-gallon plastic (HDPE) bucket. A 2-inch diameter teflon well casing was placed inside the bucket to serve as a conduit to collect water from the soil/bedrock column. Two connections were fabricated at the lid of the reactor in order to allow two lengths of tubing to be attached. One length of tubing was used to pump water out of the reactor (from the well casing) and the other to allow water to be pumped back in. Each of the two pieces of tubing had a stopcock to allow the reactor to be isolated from the atmosphere once the lid was sealed.

Assembly of the reactor, including addition of soil/bedrock samples, proceeded as follows:

- Approximately 1 L of DI water was placed in the bottom of the reactor before adding any soil/bedrock.
- The soil/bedrock samples were added in layers with additional DI water added as needed to maintain a layer of water above the top layer of the soil/bedrock column.
- Additional water was added until there was a 1/2" layer of water (approximately) on top of most of the soil/bedrock column.
- The total quantity of water added was recorded in the log book.
- The lid was placed loosely on top of the reactor and the reactor was set aside until the next morning. After allowing the reactor to sit overnight, the reactor was inspected to see if additional water needed to be added. If water was added, this was noted in the log book and the reactor was set aside until the afternoon or until the next morning. This process was repeated until no more water needed to be added. When no more water needed to be added, the reactor lid was sealed and the reactor

was placed on the bench with the other reactors. After sealing the lid, the reactor was essentially isolated from the atmosphere, except during monitoring (see below).

Reactor Monitoring: The reactors were run in the semi-batch mode. This was achieved by allowing the reactors to sit undisturbed for a period of time (usually 2 to 4 weeks), then monitoring the reactor contents by attaching the reactors to a monitoring apparatus in order to determine electrical conductivity, pH, oxidation-reduction potential (ORP), and temperature. During monitoring, water was pumped from the reactor through the pH, ORP, and conductivity cells of the monitoring apparatus and back into the reactor. The pH, ORP, and conductivity probes were in flow-thru cells so that the entire system (reactor + monitoring apparatus) was a closed system (i.e. reactor remained essentially closed off from the atmosphere, even during monitoring). The main purpose in periodically recycling the water in this manner was to monitor the progress of the mineral solubilization processes by monitoring changes in electrical conductivity over time. The periodic cycling of the water in this manner also provided some mixing of the reactor contents.

Reactor Sampling: The results collected during reactor monitoring, particularly conductivity, were recorded and graphed as monitoring progressed in order to establish how and when the reactor contents approached equilibrium. When it became evident that the reactor contents had achieved equilibrium, the reactor was scheduled for sampling at the next available opportunity. When 12 to 20 reactors were ready, particularly if all the reactors were from the same landfill or were similar materials, the reactors were sampled.

Sampling procedures were similar to the monitoring procedures described earlier, including pumping water from the reactor through pH, ORP, and conductivity cells. However, instead of allowing the water to be pumped back into the reactor, during sampling the water was pumped through a cartridge filter<sup>2</sup> into a 1000 mL polyethylene beaker. The water was transferred from the beaker into appropriate sample bottles, each containing an appropriate preservative (or no preservative). The sample bottles were submitted to an outside laboratory, BC Analytical (BCA), for analysis of the parameters listed in Table 1.

Quality Assurance/ Quality Control (QA/QC) procedures for the BCA samples included the following:

- San Jose Creek Water Quality Laboratory (SJCWQL) QA/QC staff prepared "blind" or "spike" samples containing known amounts of most of the constituents on the parameter list (Table 1). The blind samples were submitted in duplicate along with each batch of samples submitted to BCA.
- A few split samples were submitted when sufficient sample volumes were available (about 2 to 4 splits per batch). Most of the split samples were submitted only to BCA; however, in some instances, one of the pairs of the split sample was submitted to BCA and the other portion of the split sample was submitted to SJCWQL.
- If sufficient sample volume was present, BCA would perform an internal laboratory duplicate and spike analysis on one sample per batch.
- Typically for PVLF, approximately 20 samples were submitted to BCA in each batch. These 20 samples included 2 spike (blind) samples and 4 or so split samples.

Some special sample handling procedures were implemented for some of the reactors due to severe sample volume limitations. Generally, 1.0 L was required to analyze the parameters listed

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<sup>&</sup>lt;sup>2</sup> Gelman 12175 mini-capsule filter, 0.80/0.45 um pore size.

in Table 1, including sufficient sample for laboratory QA/QC (splits, spike and recovery, reanalysis of questionable or suspicious results, etc.). If less than one liter of sample is available, the laboratory had to bypass normal internal QA/QC procedures (i.e. no laboratory duplicates (splits) and no excess volume for reanalysis of suspect values). The laboratory had also been advised as to which parameters had higher priority and which parameters could be eliminated if insufficient sample volume was available to do all analyses (low priority parameters were TSS, Cyanide, and TKN -however, no parameters have to date been eliminated from any sample due to sample volume limitations).

Sufficient crushed soil/bedrock material was added to the reactors so that sufficient water volumes were available for sampling. The sample volume limitation problems resulted because some reactors did not have a sufficiently large soil/bedrock column. In these instances, the two objectives of reactor set-up came in to conflict: 1) make soil/bedrock column as large as possible vs. 2) insure, as much as possible, that reactors represent discrete conditions (i.e. try not to mix different materials together just to increase reactor mass). Of these two objectives, the latter was always given predominance; consequently, in order to represent the range of discrete conditions available for these reactors, it was necessary to create some reactors with marginal soil/bedrock and water volumes. However, cooperation and communication between the Districts and the laboratory allowed us to sample and analyze these few "sample volume limited" reactors with little or no difficulty. All remaining reactors did not require any special sample handling and no difficulties were encountered.

To date, there have not been any sample volume limitation problems for the PVLF portion of the study. Most PVLF reactors have had sample volumes above 2 or 3 L, and all have been at least at or near the 1 L minimum.

<sup>4</sup> The more soil/bedrock material added to a reactor, the more water was added to saturate the resulting soil/bedrock column. This consequently increased the amount of water available for sampling.

TABLE 1

## ACCEPTABLE DETECTION LIMITS FOR THE MINERAL LEACHING STUDY FOR ANALYSES PERFORMED AT BC ANALYTICAL

Total Suspended Solids	CONSTITUENT	EPA METHOD¹	ACCEPTABLE DETECTION LIMIT <sup>2</sup> (mg/L)	
Nitrate-Nitrogen         353.2         1.           Total Cyanide         335.2         5.           Sulfate         375.4         10.           Chloride         325.3         10.           Total Alkalinity         310.1         10.           Total Phosphate         365.4         0.5           Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barium         200.7         0.1           Aluminum         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.02           Iron         200.7         0.01           Lead         239.2         0.01           Manganese         200.7 <td>Ammonia-Nitrogen</td> <td>350.1</td> <td>1.</td> <td></td>	Ammonia-Nitrogen	350.1	1.	
Sulfate         375.4         10.           Chloride         325.3         10.           Total Alkalinity         310.1         10.           Total Phosphate         365.4         0.5           Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barium         200.7         0.1           Aluminum         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.01           Lead         239.2         0.01           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         0.05           Selenium         270.2				
Sulfate         375.4         10.           Chloride         325.3         10.           Total Alkalinity         310.1         10.           Total Phosphate         365.4         0.5           Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total COD         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         200.7         0.1           Barium         200.7         0.2           Cadmium         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.01           Lead         239.2         0.01           Manganese         200.7         0.015           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         0.01<	Total Cyanide	335.2	5.	_
Total Phosphate         365.4         0.5           Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barium         200.7         0.1           Aluminum         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.1           Lead         239.2         0.01           Manganese         200.7         0.015           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         0.05           Selenium         270.2         0.01           Silver         200.7         0.01           Sodium         200.7	Sulfate	375.4	10.	
Total Phosphate         365.4         0.5           Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barium         200.7         0.1           Aluminum         200.7         0.1           Aluminum         200.7         0.05           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.0           Iron         200.7         0.0           Lead         239.2         0.01           Manganese         200.7         0.015           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         0.05           Selenium         270.2         0.01           Silver         200.7 <td< td=""><td>Chloride</td><td>325.3</td><td>10.</td><td></td></td<>	Chloride	325.3	10.	
Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barlum         200.7         0.1           Aluminum         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.1           Lead         239.2         0.01           Manganese         200.7         0.05           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         0.05           Selenium         270.2         0.01           Sodium         200.7         0.01           Sodium         200.7         2.	Total Alkalinity	310.1	10.	
Fluoride         340.2         1.           Boron         200.7         0.05           Bromide         300.0         0.5           Total COD         410.4         5.           Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barlum         200.7         0.1           Aluminum         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.1           Lead         239.2         0.01           Manganese         200.7         0.05           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         0.05           Selenium         270.2         0.01           Sodium         200.7         0.01           Sodium         200.7         2.	Total Phosphate	365.4	0.5	
Bromide     300.0     0.5       Total COD     410.4     5.       Total Organic Carbon     415.1     0.5       Calcium     200.7     5.       Magnesium     200.7     0.1       Arsenic     206.2     0.005       Barium     200.7     0.1       Aluminum     200.7     0.2       Cadmium     213.2     0.005       Total Chromium     218.2     0.01       Copper     200.7     0.02       Iron     200.7     0.1       Lead     239.2     0.01       Manganese     200.7     0.015       Mercury     245.1     0.002       Nickel     200.7     0.05       Potassium     200.7     2.       Selenium     270.2     0.01       Silver     200.7     0.01       Sodium     200.7     2.		340.2	1.	
Total COD	Boron	200.7	0.05	
Total Organic Carbon         415.1         0.5           Calcium         200.7         5.           Magnesium         200.7         0.1           Arsenic         206.2         0.005           Barium         200.7         0.1           Aluminum         200.7         0.2           Cadmium         213.2         0.005           Total Chromium         218.2         0.01           Copper         200.7         0.02           Iron         200.7         0.1           Lead         239.2         0.01           Manganese         200.7         0.015           Mercury         245.1         0.002           Nickel         200.7         0.05           Potassium         200.7         2.           Selenium         270.2         0.01           Silver         200.7         0.01           Sodium         200.7         0.01           Sodium         200.7         2.	Bromide	300.0	0.5	
Calcium       200.7       5.         Magnesium       200.7       0.1         Arsenic       200.7       0.1         Barium       200.7       0.2         Cadmium       200.7       0.2         Cadmium       213.2       0.005         Total Chromium       218.2       0.01         Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Total COD	410.4	5.	
Magnesium       200.7       0.1         Arsenic       200.7       0.1         Barium       200.7       0.2         Cadmium       213.2       0.005         Total Chromium       218.2       0.01         Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       0.01         Sodium       200.7       2.	Total Organic Carbon	415.1	0.5	
Arsenic 206.2 0.005 Barium 200.7 0.1 Aluminum 200.7 0.2 Cadmium 213.2 0.005  Total Chromium 218.2 0.01 Copper 200.7 0.02 Iron 200.7 0.1 Lead 239.2 0.01  Manganese 200.7 0.01 Mercury 245.1 0.002 Nickel 200.7 0.05 Potassium 270.2 0.05  Selenium 270.2 0.01 Silver 200.7 0.01 Sodium 200.7 2.		200.7	5.	
Barium       200.7       0.1         Aluminum       200.7       0.2         Cadmium       213.2       0.005         Total Chromium       218.2       0.01         Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       0.01         Sodium       200.7       2.	Magnesium	200.7	0.1	
Aluminum       200.7       0.2         Cadmium       213.2       0.005         Total Chromium       218.2       0.01         Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Arsenic	206.2	0.005	
Cadmium       213.2       0.005         Total Chromium       218.2       0.01         Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Barium		0.1	
Total Chromium       218.2       0.01         Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Aluminum	200.7	0.2	
Copper       200.7       0.02         Iron       200.7       0.1         Lead       239.2       0.01         Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Cadmium	213.2	0.005	
Iron     200.7     0.1       Lead     239.2     0.01       Manganese     200.7     0.015       Mercury     245.1     0.002       Nickel     200.7     0.05       Potassium     200.7     2.       Selenium     270.2     0.01       Silver     200.7     0.01       Sodium     200.7     2.	Total Chromium	218.2	0.01	
Lead     239.2     0.01       Manganese     200.7     0.015       Mercury     245.1     0.002       Nickel     200.7     0.05       Potassium     200.7     2.       Selenium     270.2     0.01       Silver     200.7     0.01       Sodium     200.7     2.	Copper	200.7	0.02	
Manganese       200.7       0.015         Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	iron	200.7	0.1	
Mercury       245.1       0.002         Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Lead	239.2	0.01	
Nickel       200.7       0.05         Potassium       200.7       2.         Selenium       270.2       0.01         Silver       200.7       0.01         Sodium       200.7       2.	Manganese	200.7	0.015	
Potassium     200.7     2.       Selenium     270.2     0.01       Silver     200.7     0.01       Sodium     200.7     2.				
Selenium     270.2     0.01       Silver     200.7     0.01       Sodium     200.7     2.				
Silver       200.7       0.01         Sodium       200.7       2.	Potassium	200.7	2.	
Sodium 200.7 2.				
Zinc 200.7 0.03				
	Zinc	200.7	0.03	

<sup>&</sup>lt;sup>1</sup> = Aqueous digestion for metals performed using EPA Method Number 3010.

<sup>&</sup>lt;sup>2</sup> = We required the laboratory to at least achieve these detection limits. Often they were able to provide lower detection limits.