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April 10, 2000

Bruce W. Page, Ph.D.
Bruce W. Page Consulting
439 Kearney St.
El Cerrito, CA 94530

Subject: Forensic Report/Glovatorium Project

Dear Mr. Page:

The strontium and lead isotopic analyses of the six groundwater samples submitted from the Glovatorium Project have been completed. The forensic report is subdivided into a narrative section, which includes interpretations and associated figures, and appendices that discuss the analytical methods used in lead isotope analyses. Given that those who read this report may not be technical personnel, I have attempted to explain complex concepts as clearly as possible while maintaining technical accuracy. Also, note that the conclusions are based upon a limited set of samples and that, depending on the hydrogeological complexity and legal concerns surrounding this site, additional analyses may be warranted.

1.0 Introduction

The primary objectives of the forensic investigation at the Glovatorium site have been to: (1) fingerprint groundwater sources using naturally-occurring strontium isotopes (Sr; $^{87}Sr/^{86}Sr$ ratio); (2) use stable isotopes of lead (Pb; $^{206}Pb/^{207}Pb$, $^{206}Pb/^{204}Pb$, $^{208}Pb/^{206}Pb$) as tracers of dissolved phase petroleum hydrocarbons (e.g. Stoddard's Solvent); and (3) determine if there is more than one source responsible for the dissolved phase petroleum hydrocarbons. High precision strontium and lead isotope analyses are routinely used to trace chemicals of concern (COC) and, because isotopic fractionation (separation of isotopes) does not occur in these isotopic systems, isotopic ratios of any COC are retained after being released into the environment. The conservative behavior of Sr/Pb isotopes reduces the uncertainty associated with monitoring the fate/transport of COCs.

Groundwater samples provided included one upgradient well (MW-11) which may be representative of background although dissolved phase gasoline components (e.g. benzene) have been detected on occasion. Both lead and strontium isotopic ratios were analyzed in this sample. Two wells along Manila Avenue were selected for strontium isotopic analyses due to their locations. The first (GW-8) is proximal to a sanitary sewer line, which if leaking, could contribute contamination to local groundwater, while the

second (GW-3) is the most downgradient well with the highest levels of tetrachloroethylene in groundwater at the site.

The two groundwaters from wells GW-4 and GW-5 were analyzed for lead isotopic ratios to evaluate if the sources of dissolved phase petroleum hydrocarbons in GW-4 are the same as those found near the Earl Thompson tanks along 38th Street (GW-5). Similar lead isotopic ratios (e.g. agreement within ~0.2-0.3%) would suggest similar sources of TPH and Stoddard's Solvent.

2.0 Sr and Pb Isotopic Results

Analytical results and associated errors are shown in the following table:

Table of Sr/Pb Isotopic Results

Sample Number	$^{87}Sr/^{86}Sr$	Sr (ppm)	$^{206}Pb/^{207}Pb$	$^{206}Pb/^{204}Pb$	$^{208}Pb/^{206}Pb$
MW-11	0.70747	0.45	1.2134	18.987	2.0372
GW-3	0.70754	0.45	--------------Not Analyzed--------------		
GW-8	0.70748	0.62	--------------Not Analyzed--------------		
GW-4	—Not Analyzed---		1.1813	18.465	2.0721
GW-5	---Not Analyzed—		1.1962	18.684	2.0536
Error 95% CL*	0.00001	<0.5%	0.0002	0.009	0.0010

*CL = Confidence level; Pb isotopic standard is NIST/NBS SRM 981; Sr isotopic standard is NIST/NBS-987.

General discussions of the analytical methods are provided in the Appendices to this report. Differences in Sr and Pb isotope ratios are considered significant when they exceed the 95% confidence level error shown in the last row of the Table of Sr/Pb Isotopic Results.

3.0 Interpretation of Sr/Pb isotopic Results

3.1 Sr Isotopic Data

As a first approximation, given that petroleum hydrocarbons have negligible concentrations of Sr, MW-11 may be considered to represent a background sample with regard to Sr isotopic ratios and concentration. The results of the Sr analyses indicate that the Sr concentrations of the three groundwater samples are similar to each other and quite characteristic of "normal" (i.e. non-saline) groundwaters which typically have concentrations of ~0.2 to 2 ppm Sr.

The $^{87}Sr/^{86}Sr$ ratios of groundwaters from MW-11 and GW-8 are identical when analytical errors are considered. This indicates either a common source of Sr and/or suggests that the groundwater aquifer below the Glovatorium site is hydrologically continuous between these two sampling locales. Although similar, the $^{87}Sr/^{86}Sr$ of the most downgradient groundwater sample, GW-3, is slightly higher and distinct from those of the other two groundwaters. However, given the current sample population number,

and the fact that natural variations in a single, hydrologically continuous aquifer may exceed the analytical error by an order of magnitude, the most likely conclusion is that a single, hydrologically continuous aquifer exists below the Glovatorium site.

Another issue concerns the groundwater and the question of contributions, if any, from surface water. Analyses by Hurst & Associates, Inc. over the last decade have shown that the $^{87}Sr/^{86}Sr$ ratios of surface waters from the State Water Project and Metropolitan Water District of southern California range from ~0.7098 to 0.7102. These ratios are higher and distinct from those in the aquifer below the Glovatorium site. If comparisons between the Sr isotope ratios of Glovatorium site groundwater and these surface waters can be made, the isotopic differences suggest that the Glovatorium site groundwaters are not receiving major contributions from surface waters.

3.2 Lead Isotopic Data

The element lead bonds with organic compounds and is comprised of four naturally-occurring stable isotopes which can be used to discriminate among sources of petroleum hydrocarbons even at concentrations in the ppb (part per billion) range. Lead isotopic data are plotted on lead isotope discrimination diagrams in which $^{206}Pb/^{207}Pb$ is the abscissa (x-axis) and either $^{206}Pb/^{204}Pb$ or $^{208}Pb/^{206}Pb$ are the ordinate (y-axis). Petroleum hydrocarbons, whose lead isotope ratios are similar, produce clusters of data points on such plots, indicating common sources for the hydrocarbons; data points which do not form clusters are, therefore, indicative of different hydrocarbon sources. Another important point concerning lead and fingerprinting sources of hydrocarbons, is its persistence in the soil and aqueous matrices long after organic compounds have degraded.

The lead isotope results of the three groundwater samples selected and tabulated above (i.e. MW-11, potential background sample; GW-4, former Glovatorium site; and GW-5, 38th Street near Earl Thompson Tanks) are very different. For example, observed differences in the lead isotope ratios of groundwater samples GW-4 and GW-5 exceed the 95% confidence level analytical errors by the following factors: $^{206}Pb/^{207}Pb$, 75; $^{206}Pb/^{204}Pb$, 25; and $^{208}Pb/^{206}Pb$, 18.

These differences are easily visualized using lead isotope discrimination diagrams. Figures 1 and 2 below ($^{206}Pb/^{207}Pb$ versus $^{206}Pb/^{204}Pb$ and $^{208}Pb/^{206}Pb$, respectively) demonstrate the very significant differences among the lead isotope ratios of the three groundwater samples. Analytical errors are no larger than the size of each datum point.

The data indicate the presence of at least two, and possibly three, sources of petroleum hydrocarbons in these groundwaters. Given that MW-11 has shown evidence of impact by petroleum hydrocarbons, it may not be representative of background with respect to lead isotopes. With regard to the specific issues of concern at the Glovatorium site, and based upon the current data, the differences in lead isotope ratios between GW-4 and GW-5 groundwaters suggest two different petroleum hydrocarbon sources were/are involved.
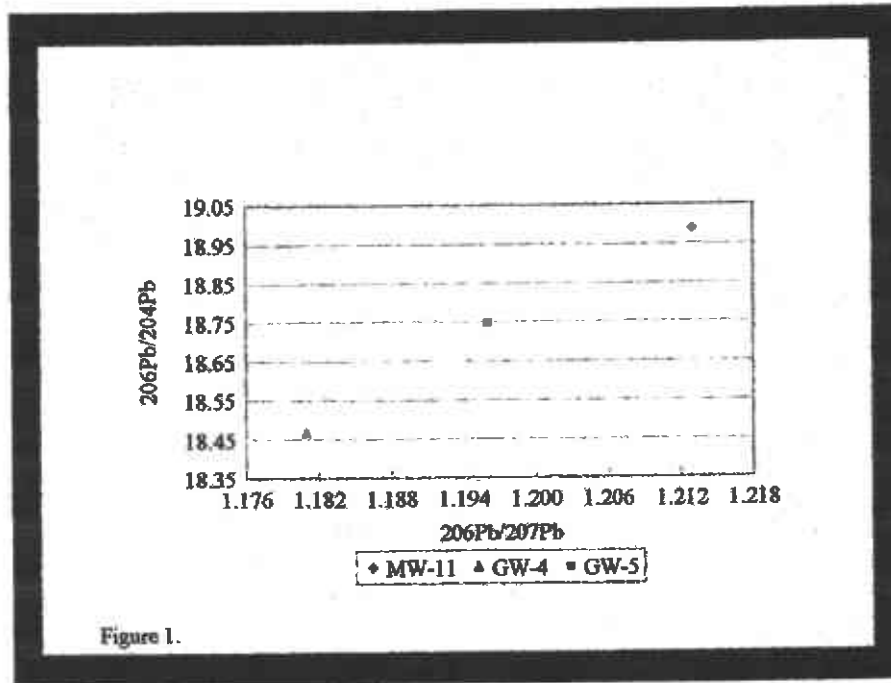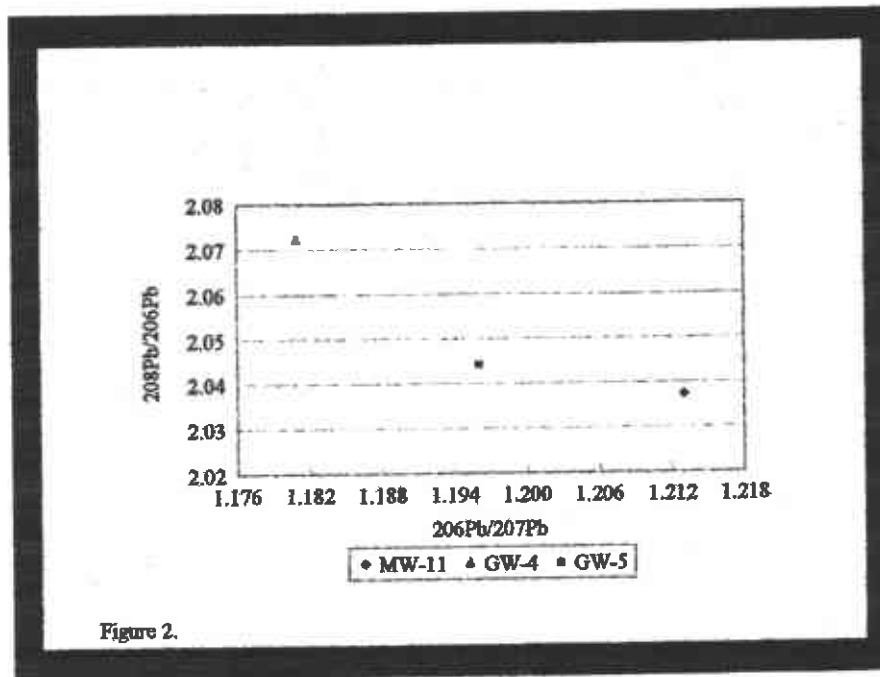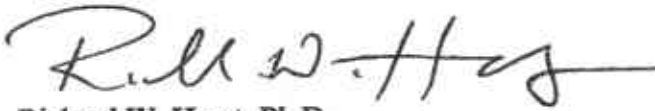
Figure 1.

Figure 2.

Thank you for the opportunity to provide our services to you and your client. We look forward to serving your environmental forensic needs in the future.

Sincerely,

Richard W. Hurst, Ph.D.
President

RWH:mah

Appendix I. Anthropogenic Lead ArchaeoStratigraphy: Estimating Ages of Hydrocarbons Releases

Dating Hydrocarbon Releases: Estimating the year a refined hydrocarbon product, such as gasoline, was released into the environment has been a difficult task. Most methods, relying upon known time periods when specific additives were used in gasoline or, in the case of mid-range crude oil distillates (e.g. diesel), presumed rates of biodegradation, frequently do not provide adequate age resolution. Furthermore, they do not provide the type of genetic information needed to correlate releases to a specific hydrocarbon source.

Lead isotopic analyses of gasoline-impacted southern California marine sediments by Patterson demonstrated the presence of systematic isotopic variations in gasoline lead between 1940 and 1978. Hurst (1991, 1996, 199, 2000) surmised that if temporal variations in gasoline lead isotope ratios could be calibrated, an improved method of age-dating gasoline releases might result. This method would have advantages over the available gasoline age-dating models in that: (1) lead does not biodegrade; (2) its isotopes do not fractionate and can be analyzed accurately by thermal ionization mass spectrometry (TIMS); (3) lead provides a long-term record of a release in the environment; and (4) lead isotopic variations of "unleaded" products provide the genetic information needed to perform release-source correlations.

Acquiring samples to evaluate whether or not a calibration curve could be developed had, as its primary concern, the acquisition of leaded gasolines and gasoline-impacted soils whose ages, of production or contamination respectively, were accurately known. Samples selected for analysis included: documented, archived leaded gasolines from refineries; gasoline-impacted soil horizons which were radiometrically dated; and gasoline-impacted soil horizons with documented environmental releases (e.g. HazMat team responses). To date, 86 samples throughout the United States have been analyzed using ultraclean chemistry techniques, followed by high precision lead isotope ratio analyses ($^{206}Pb/^{207}Pb$; $^{206}Pb/^{204}Pb$; $^{206}Pb/^{208}Pb$; analytical errors $\leq 0.05\%$.) via TIMS.

The lead isotope analyses have produced a well-defined calibration curve termed the ALAS Model (Anthropogenic Lead ArchaeoStratigraphy) which is used to estimate the age of a release of leaded gasolines. ALAS Model lead isotope ratios are reported using a "delta notation" as employed in light stable isotope analyses (e.g. CHONS). The reference lead isotope ratio is Present Day Average Earth Crustal Lead in which $^{206}Pb/^{207}Pb$ equals 1.1966. This choice is convenient because it is identical to measured $^{206}Pb/^{207}Pb$ ratios of ALAS calibration samples in 1975, the year that marked the beginning of EPA mandated decreases in gasoline lead concentrations.

Systematic increases in $\delta^{206}Pb$ observed in the ALAS Model curve (1960 - 1990) were caused by the progressive increased use of radiogenic lead from Mississippi Valley-Type ores ($^{206}Pb/^{207}Pb \approx 1.30$) in the production of alkyllead additives, in preference to less radiogenic, geologically older ores from both foreign and domestic sources ($^{206}Pb/^{207}Pb < 1.1$). The lack of scatter evident in the ALAS Model calibration curve is attributed to the use of the same sources and proportions of sources of lead by the major alkyllead manufacturers (e.g. Ethyl Corporation, DuPont) from 1960 through 1990.

. Evidence contradicting this hypothesis has been sought but not found; the correlation between the ALAS Model Age and Documented Age of releases from actual site remediation studies ($R^2 = 0.97$) supports the proposed hypothesis.

Since 1992, there have been more than 50 applications of the ALAS Model to site remediation investigations involving gasoline, diesel, kerosene, and motor oils throughout the United States. Successful dating of mid-range and higher distillates is attributed to accidental additions of lead additives, perhaps through common transfer lines, during refining. Case studies involving single and multiple releases of hydrocarbons in California and Illinois respectively will be used to demonstrate the effectiveness of this technique in environmental site remediation.

Unleaded Hydrocarbons: The term "unleaded", as applied to gasolines produced over the last decade, or to any crude oil distillate fraction to which lead was never added, is a misconception. All hydrocarbons contain lead inherited from their crude oil sources, at levels typically in the tens of ppb range. This is enough lead for high precision isotopic analyses by TIMS. Observed variations in lead isotope ratios of different refiner's unleaded products allow suspected sources to be identified and quantified in cases where plumes have commingled.

MTBE and BTEX: Tracing dissolved phase gasoline components (MTBE, BTEX) using lead isotopes is also viable. Results of unleaded gasoline - aqueous exchange reactions performed in collaboration with MIT indicate that organic lead is initially, and rapidly, transported into the aqueous phase during solvation of MTBE, with longer term transport accomplished via less soluble BTEX compounds. Since lead isotopes do not fractionate, the unique lead isotopic signature of the gasoline is carried into the aqueous phase, allowing the source(s) of the MTBE/BTEX to be evaluated. The laboratory data are supported by observed lead isotopic equilibrium between free product and impacted groundwater at remediated sites throughout the U.S.

Appendix II. Analytical Procedures

Lead Isotope Analyses by Thermal Ionization Mass Spectrometry (TIMS):

The description of sample preparation, ion exchange chromatography, and thermal ionization mass spectrometry is a general description of typical procedures used to analyze samples for high precision lead isotope ratios. More specific, technical details have been omitted, in part, for brevity, for clarity to nontechnical readers, and also, because variations in sample matrices/chemistry may require slight modifications to the procedures described below.

1. Sample Preparation:

Soils: Approximately 0.25 grams of soil are weighed into a precleaned quartz or TFE teflon beaker. Depending on the nature of lead speciation, lead is extracted via sequential chemical extractions which can include n-pentane (organolead present), 0.1 N HCl, 50% aqua regia, warm H_2O_2 plus 8N HNO_3, and hot HF. Selection of which combination and duration of each extraction step are dependent on the nature of the soil matrix and age/speciation of adsorbed anthropogenic lead (if known). Following the extraction, the leachate is transferred via HDPE pipettes to a clean, preweighed quartz/TFE teflon beaker. The leachate solution is weighed and a known amount of ^{205}Pb tracer is added if concentration determination by isotope dilution mass spectrometry (IDMS) is to be performed. The leachate is then evaporated to dryness.

Aqueous and Liquid Organic (e.g. Gasoline) Phases: Approximately 10 to 100 ml of liquid phase are weighed into a precleaned quartz beaker. Aqueous phases may be spiked with ^{205}Pb for concentration determination. Liquid organic phase samples may either be extracted using dilute HCl or the entire sample may be processed. In both cases, the liquid phase is evaporated to dryness. The beaker is carefully rinsed down with HNO_3, and the resulting solution spiked with ^{205}Pb tracer if IDMS is to be performed. The solution is evaporated to dryness.

2. Ion Exchange Chromatography

Lead is separated from other elements which may interfere with the measurement of naturally-occurring lead isotopes (^{204}Pb, ^{206}Pb, ^{207}Pb, ^{208}Pb) using ion exchange chromatography. Potential interferences in high precision lead isotope analyses may arise from instabilities in the TIMS ion current (chemically-induced interference) and/or isobaric mass overlaps.

Use of AG 1X8 anion exchange or crown ether resins allows lead to be efficiently removed from other elements (>99+% purity), eliminating interferences caused by ion current instability and isobaric overlaps. Employing different acids of different normalities either causes lead ions to be preferentially retained on (e.g. 1N HBr, 3.1N HCl) or removed from (e.g. 6.2 N HCl) the resin relative to other ions. The resulting

solution containing the high purity lead from a specific sample is evaporated to dryness in preparation for isotopic composition analysis by TIMS.

3. Thermal Ionization Mass Spectrometry (TIMS):

Sample Loading: The high purity lead samples are redissolved in ~0.04 ml 0.75N H_3PO_4 using a micro-pipette. A drop of the redissolved lead sample and silica gel substrate are placed on a 30 micron thick precleaned rhenium filament which has been mounted to a filament holder. A low current is run through the filament to thoroughly dry the sample and fuse the silica gel. Typically 12 to 24 samples are then placed in a multi-sample turret which is placed into the TIMS.

Lead Isotope and Concentration Analysis: Each sample in the multi-sample turret is sequentially rotated into the TIMS source for lead isotopic analysis. Individual sample analyses for lead isotopic composition (IC) involve 100 to 200 scans of the four naturally-occurring lead isotopes, with each run requiring 1 to 2 hours. Lead concentration by isotope dilution mass spectrometry (IDMS) may either require a separate run if a ^{206}Pb spike is used or may be performed with the IC run if an ultrapure ^{205}Pb spike is available. Internal precisions for lead isotope ratios are < 0.1% at the 95% confidence level.

Because TIMS analyses result in lead isotopic fractionation, each sample's IC and ID ratios are corrected for fractionation using NIST SRM 981, a lead isotopic standard. Corrections for lead isotopic fractionation are 0.12% $\pm$ 0.03% per atomic mass unit. Overall accuracy in lead isotopic ratios after fractionation corrections is typically $\leq \pm$ 0.05% for $^{206}Pb/^{207}Pb$ and < $\pm$ 0.1% for $^{208}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$. Errors in lead concentrations by IDMS range from < 1% at the ppm level to ~20% when lead concentrations are in the sub-ppb (picogram/gram) range. As is the case with all high precision isotopic methods, natural isotopic heterogeneity in samples may exceed the analytical errors.

4. Total Procedural Blanks

Total lead blanks for the entire sample preparation and loading process are ≤ 20 picograms (0.020 nanograms). This amount is negligible relative the total lead present in each sample.

Appendix III. Strontium Isotopes as Tracers of Contaminants in Groundwater

Strontium (Sr) has four naturally occurring isotopes. These are strontium 84, strontium 86, strontium 87, and strontium 88. Strontium 87 is produced from the decay of a naturally occurring radioactive isotope, rubidium 87. Because the amount of rubidium 87 differs in various rocks and minerals, there is a variation in the amount of strontium 87 in these same rocks and minerals. Furthermore, because strontium 87 is the only isotope of strontium produced by radioactivity decay, the ratio of strontium 87 to strontium 86 will increase over time. Interactions between groundwater and rocks and minerals will result in an equilibrium whereby the groundwater ratio of strontium 87 to strontium 86 is established. Our ability to precisely measure these isotope ratios allows us to discriminate one groundwater from another.

When a contaminant finds its way into the groundwater, the strontium it carries with it will change the isotope ratio of strontium in the groundwater. The result will be that the strontium isotopic ratio of the groundwater will now lie between that of the original groundwater and that of the contaminant. Using a well designed sampling program and isotope mixing models, it becomes possible to evaluate the amount of the contaminant, and frequently the source of the contaminant, in the groundwater. The latter can be accomplished by integrating the isotopic results with other geotechnical data, such as groundwater modeling and other geochemical data.

Recent applications of strontium isotopic data include investigations of seawater intrusion, the evaluation of sources of nitrates in groundwater, and the study of chlorinated solvent contamination in groundwater. In the case of chlorinated solvents, it has been observed that their addition to groundwater changes the strontium isotopic ratio of the groundwater and also their introduction into groundwater changes the way groundwater interacts with rocks and minerals. This has allowed us to monitor the fate and transport of chlorinated solvents in groundwater. We have also seen that there are excellent correlations between strontium isotopes and the ratios of one chlorinated solvent to another. Case studies in Missouri, Carolina, and California indicate strontium has the potential to serve as a surrogate tracer of chlorinated solvents in the environment.

In conclusion, Hurst & Associates Inc., continues to pursue research in the use of strontium isotopes, as well as other geochemical and statistical techniques, to better understand how we may trace contaminants through the environment. On a broader scale, our objectives also include the development of techniques to identify responsible parties in cost-recovery litigation and reduce the uncertainties associated with risk based corrective action (RBCA) modeling.